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Physical Chemistry of Ionic Liquids

Guest Editor: Frank Endres (Technical University of Clausthal, Germany)

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Nitrile-functionalized pyrrolidinium ionic liquids as solvents for cross-coupling reactions involving *in situ* generated nanoparticle catalyst reservoirs†

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A series of nitrile-functionalized pyrrolidinium-based ionic liquids have been prepared and characterized by spectroscopic methods and X-ray crystallography. The application of these new ionic liquids as reaction media for Suzuki and Stille C–C cross-coupling reactions has been investigated and compared with related imidazolium and pyridinium systems (including those with and without nitrile functionalities). The nature of the ionic liquid strongly influences the catalyzed reaction and it would appear that, in addition to the nitrile group, the strength of anion–cation pairing in the ionic liquid and the viscosity of the ionic liquid play critical roles. Nanoparticles are also detected following catalysis and their role, and the influence of the ionic liquid on them, is assessed. The ability to use the nitrile-functionalized pyrrolidinium-based ionic liquids diluted in other (non-functionalized) ionic liquids is also described.

Introduction

Ionic liquids (ILs) are fascinating compounds with unique properties that could have advantages over conventional solvents in synthesis and catalysis.[1] Functionalized ILs, also frequently referred to as task specific ILs and first described by Davis *et al.*,[2] have significantly broadened the scope of these potential applications. Although the design and synthesis of functionalized ILs has been intensively investigated since their introduction in 2001, the majority of studies have been based on imidazolium systems.[3,4] ILs with functional groups attached to other cations, such as pyrrolidinium, pyridinium and ammonium systems, have received considerably less attention.[5–7] The reason for the dominance of imidazolium-based systems is partly historical and partly because the reaction of alkyl imidazole (usually 1-methylimidazole) with alkyl halides bearing a functional group tends to give the desired functionalized IL product in high yield.

Designing an IL to be used as a solvent for a specific reaction requires a mechanistic understanding of the reaction in question. However, mechanistic studies of reactions in ILs are quite rare,[8] although it is clear that there should be an optimum combination of cations and anions for an IL with a specific function, that in the case of a catalyzed reaction, facilitates the solvation of the catalyst and reagents and the formation and stabilization of the active catalytic species. C–C coupling reactions have been extensively investigated in IL,[9] and as in molecular solvents,[10] there is evidence to suggest the formation of the palladium nanoparticles is important.[11,12] C–C coupling reactions involving aryl iodides and activated bromides can be promoted by almost any Pd catalyst precursor in molecular solvents,[10,13] and in ILs.[5,6,9] Moreover, ILs with functional groups attached to the cation are able to stabilize and/or activate the *in situ* formed palladium nanoparticles, which act as palladium(0) reservoirs, ultimately facilitating coupling reactions. The nature of the IL anion also plays an important role in the outcome of the catalytic processes[14] with anions that strongly interact with nanoparticle surfaces impeding the loss of Pd(0) and hence reducing catalytic activity in C–C coupling reactions. Indeed, a critical balance between nanoparticle reactivity and stability must be found in order to achieve high turnover numbers.

Previously, we have reported imidazolium and pyridinium-based ILs with nitrile functionalities and we found these ILs can serve as both solvent and stabilizer for palladium nanoparticle reservoirs in certain C–C cross-coupling reactions.[6,15–17] In comparisons between these nitrile-functionalized ILs and their non-functionalized counterparts, in various coupling reactions, a reduction in palladium leaching combined with an increase in catalyst stability was found to lead to considerably higher catalytic turnover numbers in the functionalized solvents. Herein, we report the synthesis of a series of nitrile-functionalized pyrrolidinium ILs that have so far been overlooked, and study their ability to facilitate Suzuki and Stille C–C cross-coupling reactions in the presence of simple palladium

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sources and weak inexpensive bases. In addition, the possibility to use the nitrile-functionalized pyrrolidinium-based ILs diluted in other (non-functionalized) ILs is also described.

Results and discussion

The reaction of stoichiometric amounts of butylnitrile pyrrolidine with the appropriate alkyl iodide (alkyl = methyl, ethyl, propyl and butyl) affords the pyrrolidinium iodides **1a–4a** in quantitative yield (Scheme 1). Metathesis of the iodide salts with lithium bis[(trifluoromethyl)sulfonyl]imide, Li[Tf_2N], gave the corresponding room temperature ILs **1b–4b**. The known butylnitrile-functionalized imidazolium and pyridinium salts (**5a**, **5b**, **6a** and **6b** in Scheme 1) were also prepared, for comparison studies described below, according to literature procedures.[6,18]

The ^{1}H-NMR spectra of all the pyrrolidinium salts, **1–4**, in CD_2Cl_2, are as expected. The CH_2 groups adjacent to the N-atom in the pyrrolidinium ring appear as overlapping multiplets in the range 2.5–3.8 ppm, with the remaining CH_2 groups observed between 0.9 and 1.6 ppm. The only well resolved signal emanates from the CH_2 unit adjacent to the nitrile group which gives a clear J_{HH} value of 7.0 Hz in all cases. The $C{\equiv}N$ bond vibrations in the IR spectra of the pyrrolidinium iodides, **1a–4a**, are in the range 2244–2247 cm^{-1}; and in the [Tf_2N]-based ILs **1b–4b**, they are observed between 2251 and 2253 cm^{-1}. It is noteworthy that the vibration of **1a** (2244 cm^{-1}) is almost the same as in the imidazolium-based iodides **5a** (2243 cm^{-1}) and **6a** (2245 cm^{-1}), indicating that the $C{\equiv}N$ bond strength, and hence the basicity of the N-atom lone pair, in the different cations are equivalent. Similarly, the absorption of the $C{\equiv}N$ bond in the [Tf_2N]-based IL **1b** (2250 cm^{-1}) is very close in value to the imidazolium salt **5b** (2252 cm^{-1}).

The pyrrolidinium iodides **1a–4a** are hydrophilic solids at room temperature with only **4a** melting below 100 °C and therefore corresponding to an IL according to the widely used definition (Table 1).[19] Moreover, the Tf_2N-based ILs **1b–4b** are all more viscous than the structurally related ILs **5b** and **6b**.[6,18]

Crystals of **1a** suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether into an acetonitrile solution containing the salt. The structure of **1a** is shown in Fig. 1 and key bond parameters are listed in the caption. The $C{\equiv}N$ bond length in **1a** [1.147(5) Å] is very similar to that observed in **5a**,[18] and other imidazolium[15] and pyridinium[6] salts with nitrile substituents, corroborating the inferences made from the IR spectra. All other bond parameters of the cation are essentially as expected.

Table 1 Melting points of **1a–6a** and viscosities of **1b–6b**

Melting points of iodides/°C	Viscosities of Tf_2N ILs at 20 °C/cP
1a: 138	**1b**: 359
2a: 190	**2b**: 440
3a: 142	**3b**: 415
4a: 60	**4b**: 716
5a: 69[12]	**5b**: 168[12]
6a: 101[7]	**6b**: 169

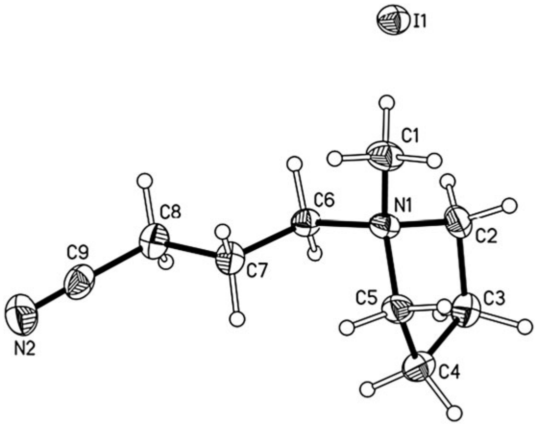
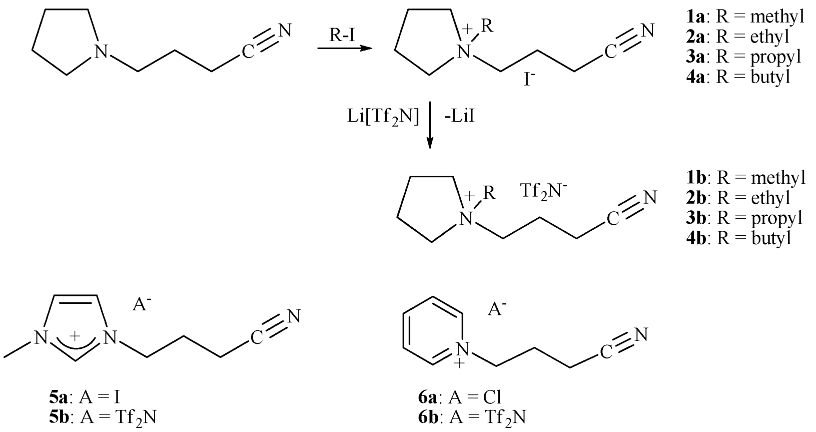


Fig. 1 Solid state structure of **1a**. Key bond lengths (Å) and angles (°): N(1)–C(1) 1.497(5), N(1)–C(5) 1.509(5), N(1)–C(2) 1.516(5), N(1)–C(6) 1.521(5), N(2)–C(9) 1.147(5). C(1)–N(1)–C(5) 112.2(3), C(1)–N(1)–C(2) 112.0(3), C(5)–N(1)–C(2) 101.7(3), C(1)–N(1)–C(6) 109.6(3), C(5)–N(1)–C(6) 112.8(3), C(2)–N(1)–C(6) 108.2(3). Ellipsoids are drawn at the 50% probability level.

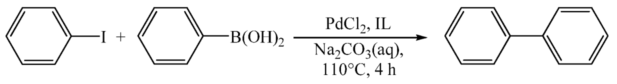
Application of 1b–4b in cross-coupling reactions

Carbon–carbon cross-coupling reactions have been extensively studied in imidazolium,[20] phosphonium,[21] pyrrolidinium[22]



Scheme 1 ILs with nitrile functionalities employed in this study.

Table 2 Suzuki coupling of iodobenzene and phenylboronic acid[a]



Entry	IL	Yield (%)
1	**1b**	77
2	**2b**	71
3	**3b**	69
4	**4b**	67
5	**5b**	85
6	**6b**	86
7	[emim][Tf$_2$N][b]	72
8	[omim][Tf$_2$N][c]	41
9	**1b**: [emim][Tf$_2$N], 1 : 9	78
10	**1b**: [emim][Tf$_2$N], 5 : 5	75
11	**1b**: [emim][Tf$_2$N], 9 : 1	73
12	**4b**: [emim][Tf$_2$N], 9 : 1	68
13	**5b**: [emim][Tf$_2$N], 5 : 5	70
14	**1b**[d]	76
15	**4b**[d]	70

[a] Conditions: a mixture of the iodobenzene (0.5 mmol), phenylboronic acid (0.55 mmol), Na_2CO_3 (1.05 mmol in 0.5 ml H_2O) and $PdCl_2$ (0.006 mmol) in IL (1.0 ml) was heated at 110 °C for 4 h. Yields correspond to biphenyl product determined by GC. [b] [emim] = the 1-ethyl-3-methylimidazolium cation. [c] [omim] = the 1-octyl-3-methylimidazolium cation. [d] Using pre-formed palladium nanoparticles in place of $PdCl_2$ (see Experimental).

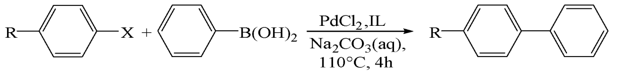
and ammonium[23] based ILs. In general the reported yields of the products tend to be high in the presence of palladium complexes with phosphine or carbene ligands. In contrast, due to the presence of the nitrile group in the functionalized ILs described herein, simple palladium salts can be used as pre-catalysts, as the nitrile group weakly coordinates to the Pd-centre helping to stabilize catalytic intermediates. Moreover, Pd nanoparticles have been observed in some instances in functionalized ILs, presumably forming in a pre-catalytic step, and serve as the source of the active mononuclear catalyst.

Initial screening of ILs **1b–4b** as solvents in Suzuki reactions indicated all these ILs can be used together with $PdCl_2$, and an aqueous solution containing the base, that combines to form a homogeneous reaction medium (see Table 2). Employing the same conditions, the imidazolium and pyridinium-based ILs **5b** and **6b** were also screened so that direct comparisons could be made as different conditions were used in previous studies.[6,17]

The yields of the coupling product isolated from the reactions between iodobenzene and phenylboronic acid in the nitrile-functionalized pyrrolidinium ILs **1a–4b** (entries 1–4, Table 2) are all slightly lower than in the imidazolium-based IL **5b**[24] and the pyridinium-based IL **6b**[6] (entries 5 and 6, Table 2). The influence of the different ILs on the yield of the biphenyl product can be explained by the differences between the properties of the IL used. Since IR spectroscopy (and X-ray structural data) suggests a comparable basicity of the N-atom of the nitrile group in imidazolium and pyrrolidinium-based ILs the differences in product yields observed in ILs **1b–6b** must be attributed to other factors.[25] One of the most significant differences in the properties of **1a–4b** and **5b** and **6b** corresponds to their viscosities. A plausible reason for the decreased yield of the Suzuki reaction in **1a–4b** than in **5b** and **6b** could be the higher viscosities of the pyrrodinium ILs of **1a–4b** which impedes the interaction between the substrate and the catalyst, and the lower viscosity of **5b** and **6b** favoring faster mass-transfer and increasing the interactions between the substrates and the catalyst. Indeed, as the viscosity increases from **1b** to **4b**, the yield of the product also decreases (entries 1–4, Table 2). To confirm this hypothesis, Suzuki reactions in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide ([emim][Tf$_2$N]) and 1-octyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([omim][Tf$_2$N]) were conducted. These ILs have a similar chemical structure but differ significantly in their viscosity.[18,26] In the least viscous IL, [emim][Tf$_2$N], the yield is higher than in the most viscous IL, [omim][Tf$_2$N], where the yield is very low (entries 7 and 8, Table 2). The influence of the viscosity can be ascertained if binary mixtures of ILs **1b**–[emim][Tf$_2$N] and **4b**–[emim][Tf$_2$N] are used. IL [emim][Tf$_2$N] has a low viscosity (about 28 cP at room temperature[18]) and the viscosity of [omim][Tf$_2$N] is about 93 cP at room temperature.[26] Addition of [emim][Tf$_2$N] to **1b** modulates the overall viscosity of the system. In a mixture of **1b**–[emim][Tf$_2$N] containing higher volume ratio of [emim][Tf$_2$N], *i.e.* with a lower overall viscosity, the yield of the biphenyl is higher. However, as the volume concentration of the more viscous IL **1b** increases from 10 to 90% v/v, the viscosity of the **1b**–[emim][Tf$_2$N] mixture changes from *ca.* 50 cP to *ca.* 350 cP, and the yield decreases gradually from 78% to 73% (entries 9–11, Table 2). Addition of 10% v/v of [emim][Tf$_2$N] to **4b** results only in a small decrease in viscosity of the reaction mixture, and yield of the biphenyl remains essentially unchanged (entry 12, Table 2).

Suzuki coupling reactions using bromobenzene and chlorobenzene were evaluated in **1b** and **4b** under the same conditions and, as expected, the yield of the reaction between bromobenzene and phenylboronic acid is significantly lower

Table 3 Suzuki coupling of various aryl halides with phenylboronic acid[a]



Entry	Aryl halide	IL	Yield (%)
1	R = H, X = Br	**1b**	20
2	R = H, X = Cl	**1b**	1
3	R = H, X = Br	**4b**	31
4	R = H, X = Cl	**4b**	1
5	R = CN, X = I	**1b**	99
6	R = CN, X = Br	**1b**	95
7	R = NO_2, X = I	**1b**	99
8	R = NO_2, X = Br	**1b**	98
9	R = OMe, X = I	**1b**	65
10	R = CN, X = I	**4b**	98
11	R = CN, X = Br	**4b**	96
12	R = NO_2, X = I	**4b**	99
13	R = NO_2, X = Br	**4b**	98
14	R = OMe, X = I	**4b**	61

[a] Conditions: a mixture of the aryl halide (0.5 mmol), phenylboronic acid (0.55 mmol), Na_2CO_3 (1.05 mmol in 0.5 ml H_2O) and $PdCl_2$ (0.006 mmol) in IL (1.0 ml) was heated at 110 °C for 4 h. Yields correspond to the biphenyl product determined by GC.

than those using iodobenzene, and with chlorobenzene the system is essentially inactive (entries 1–4, Table 3). ILs **1b** and **4b** were also evaluated as solvents for coupling reactions between activated aryl iodides and bromides and phenylboronic acids. However, the yield of the biphenyl products differs only slightly since activated aryl halides were used. High yields can be obtained under the same reaction conditions (entries 5–14, Table 3). For the de-activated substrate, *p*-methoxyiodobenzene, the yield of the product is still reasonable with the iodide precursor (entries 9 and 14, Table 3).

Coordination of the nitrile group in the functionalized ILs to the Pd(II) centre facilitates the solvation of the $PdCl_2$ in **1b–4b**. In all the reactions listed in Tables 2 and 3 the orange solution rapidly turns black, and in the reactions where the conversion is high, the solution subsequently becomes orange. In contrast, in the low yielding reactions the solution remains black. Similar observations have been noted elsewhere,[17] and have been attributed to the initial formation of palladium nanoparticles (black solution) which serves as a source of the actual Pd(II) catalyst (orange solution) following oxidative addition of the aryl halide substrate to a Pd atom on the surface of the nanoparticle. Consequently, pre-formed Pd nanoparticles were evaluated in place of $PdCl_2$ in the Suzuki reaction between iodobenzene and phenylboronic acid and approximately the same yield was obtained (entries 14 and 15, Table 2) irrespective of the Pd source used.

Previously, palladium nanoparticles generated *in situ* in ILs have been isolated and characterized by transmission electron microscopy (TEM).[27–29] Palladium nanoparticles have also been pre-prepared and dispersed in ILs and then used to catalyze various reactions.[13,30,31] Typically, the size of the palladium nanoparticles isolated from the reactions range from *ca.* 2–5 nm, although smaller nanoparticles, *ca.* 1 nm,[32] and larger ones of *ca.* 7–8 nm, have also been observed.[33] While the nanoparticles are firmly believed to act as catalyst reservoirs in C–C coupling reactions, aggregation of the nanoparticles can occur, causing a decrease in catalytic activity,[21–23] due to a lower number of accessible surface palladium atoms thereby reducing the amount of the active catalyst that can be generated. Indeed, nitrile-functionalized ILs help to prevent nanoparticle aggregation, presumably due to weak but stabilizing interactions between the nitrile groups of the IL and the surface of the nanoparticles, in addition to stabilization by the IL anion.[6,14,17]

In order to establish the size of the nanoparticles formed at the early stages of the coupling reaction, the reaction between phenylboronic acid and iodobenzene in **1b** was quenched after 15 minutes, and the nanoparticles were extracted into ethanol. TEM reveals that the nanoparticles have a size range of 3.5–10.5 nm (Fig. 2), and are more heterogeneous in nature than those prepared by reduction of palladium complexes, *e.g.* $PdCl_2$, $Pd(cod)Cl_2$ and $Pd_2(dba)_3$, with hydrogen in $[bmim][PF_6]$,[28,29] and also show a greater size distribution to those isolated from Stille reactions using imidazolium and pyridinium-based ILs **5b** and **6b**.[6,17]

A series of Stille coupling reactions were also carried out in ILs **1b–4b** using palladium chloride as a pre-catalyst (Table 4). ILs **1b–4b** prove to be excellent solvents for Stille reactions. In contrast to Suzuki reactions where the low viscosity of the IL **1b** contributes positively to the higher yield of the biphenyl, the highest yields in Stille reactions were obtained in the most viscous IL, *i.e.* **4b**. Notably, the yields of the styrene product obtained in **1b–4b** are superior to those obtained in **5b** and **6b**.[6,17] Control experiments using $[emim][Tf_2N]$ and $[omim][Tf_2N]$ also showed that in the latter IL, *i.e.* the most viscous of the pair, a higher yield of the styrene product is obtained (entries 7 and 8, Table 4). Similar yields are observed if mixtures of **1b** or **4b** with $[omim][Tf_2N]$ are used in the coupling reaction (data not shown). In addition, if the $PdCl_2$ pre-catalyst is replaced by pre-formed palladium nanoparticles, the yield of the coupling reactions is essentially unchanged (entries 9 and 10, Table 4). Despite the improvement imparted by ILs **1b–4b** compared to other imidazolium-based ILs they do not provide good yields when bromobenzene and chlorobenzene substrates are used, although excellent yields are obtained with activated aryl bromides (entries 13 and 16, Table 4). Binary IL mixtures composed of **4b** and $[omim][Tf_2N]$ have been used as solvents for the Stille reaction between phenylboronic acid and iodobenzene (entries 17–19, Table 4). Although the yield of the styrene is higher than that obtained in $[omim][Tf_2N]$ they are almost the same as the yield obtained in **4b**.

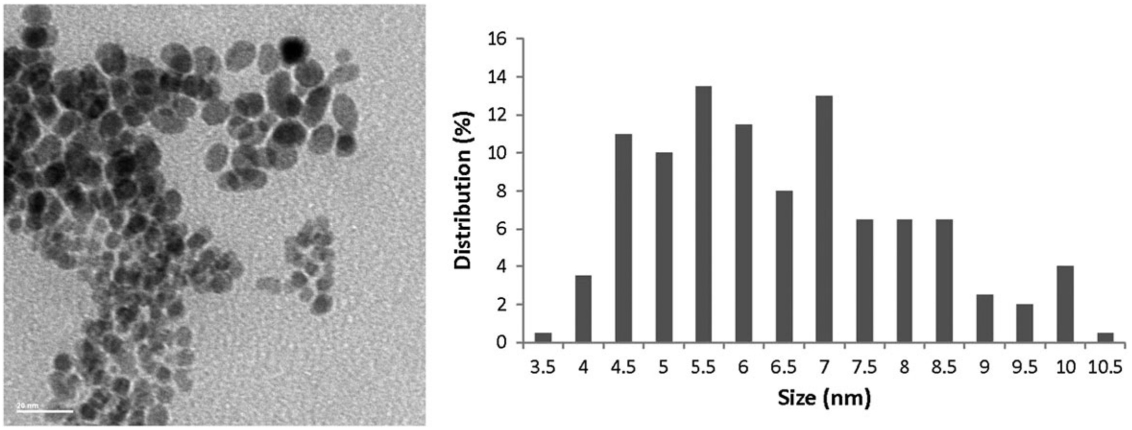
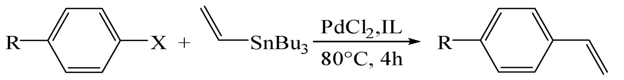


Fig. 2 TEM image and size distribution of palladium nanoparticles generated *in situ* in the Suzuki reaction between iodobenzene and phenylboronic acid in **1b** (quenched after 15 minutes).

Table 4 Stille coupling of various aryl halides with tributylvinylstannane[a]



Entry	Aryl halide	ILs	Yield (%)
1	R = H, X = I	**1b**	75
2	R = H, X = I	**2b**	70
3	R = H, X = I	**3b**	91
4	R = H, X = I	**4b**	92
5	R = H, X = I	**5b**	54[34]
6	R = H, X = I	**6b**	54[6]
7	R = H, X = I	[emim][Tf$_2$N][b]	66
8	R = H, X = I	[omim][Tf$_2$N][c]	82
9	R = H, X = I	**1b**[d]	73
10	R = H, X = I	**4b**[d]	86
11	R = CN, X = I	**1b**	99
12	R = NO$_2$, X = I	**1b**	99
13	R = CN, X = Br	**1b**	91
14	R = CN, X = I	**4b**	99
15	R = NO$_2$, X = I	**4b**	99
16	R = CN, X = Br	**4b**	88
17	R = H, X = I	**4b**: [omim][Tf$_2$N], 9 : 1	90
18	R = H, X = I	**4b**: [omim][Tf$_2$N], 5 : 5	91
19	R = H, X = I	**4b**: [omim][Tf$_2$N], 1 : 9	90

[a] Conditions: a mixture of the aryl halide (0.5 mmol), tributylvinylstannane (0.6 mmol), PdCl$_2$ (0.025 mmol) in IL (1.0 ml) was heated at 80 °C for 4 h. Yields correspond to the biphenyl product determined by GC. [b] [emim] = the 1-ethyl-3-methylimidazolium cation. [c] [omim] = the 1-octyl-3-methylimidazolium cation. [d] Using pre-formed palladium nanoparticles in place of PdCl$_2$ (see Experimental).

Stille reactions in ILs have previously been shown to involve palladium nanoparticles and ILs[6,17] **1b–4b** are no exception. Unlike Suzuki reactions in which the initially formed palladium nanoparticles disappear, the reaction mixtures with tributylvinylstannane turn black quickly indicating the formation of nanoparticles, and the particles appear to persist throughout the entire reaction. Nanoparticles were isolated after 15 minutes from the reaction between iodobenzene and tributylvinylstannane in **4b**, by extraction into ethanol, and characterized using TEM (Fig. 3). The nanoparticles range in size from 3.5 to 8.0 nm, not too dissimilar to those isolated from the Suzuki reaction and similar in size to nanoparticles observed in nitrile-functionalized imidazolium and pyridinium-based ILs.[6,17] However, the size distribution is slightly different, with majority of the nanoparticles being in the range of 5.0–6.0 nm.

The differences in product yields observed in ILs **1b–6b** must be attributed to the different bulk physico-chemical properties of these ILs (viscosity, cohesive pressure and so on) and/or to the different ability of the cationic and anionic moiety to give specific interactions with the dissolved species. It is known that ILs are able to form ionic organized networks in the solid, liquid and gas phase, which not only determine most of the unique physico-chemical properties of these media (such as their electrical conductivity, polarity, solubility) but also affect through specific effects the kinetic and thermodynamic behavior of reactions performed in them.[25] Although the [Tf$_2$N]$^-$ anion can be classified as a weakly interacting anion and the ILs containing this counteranion tend to have a relatively low charge ordering (*i.e.*, the ionic network is more 'liquid-like'), the cationic portion also determines the strength and topology of cation–anion contacts. Recent high-energy X-ray diffraction experiments[35] suggest that the intermolecular interaction between [emim]$^+$ and [Tf$_2$N]$^-$ is stronger than that involving the *N*-methyl-*N*-propylpyrrolidinium cation, and analogously, ESI-MS measurements indicate the following qualitative order of intrinsic bond strength to [Tf$_2$N]$^-$: [emim]$^+$ > [bmim]$^+$ > [bpy]$^+$ (py = pyridinium) > [bmpyrr]$^+$ (pyrr = pyrrolidinium).[36] Therefore, on progressing from imidazolium to pyrrolidinium salts the reduced cation–anion interaction increases the competitive ability of anion or cation to interact with dissolved species. It has previously been shown that coordinative expansion at the tin atom by nucleophiles in Stille reactions is important,[37] thus the positive effect of the pyrrolidinium salts on the Stille reaction may be ascribed to a 'nucleophilic assistance' effect of the more weakly interacting [Tf$_2$N]$^-$ anion in the transmetallation step. This effect is not present in the Suzuki reaction, where the boronic acid is activated by the added base, the rate of dissolution of which might be reduced at higher viscosities. In contrast, in Stille reactions where the nanoparticles are more persistent, the higher viscosities might further facilitate nanoparticle-based processes.

It was possible to re-use the IL–catalyst system in Suzuki reactions five times without a decrease in activity. Moreover, under analogous conditions poor recycling is observed in

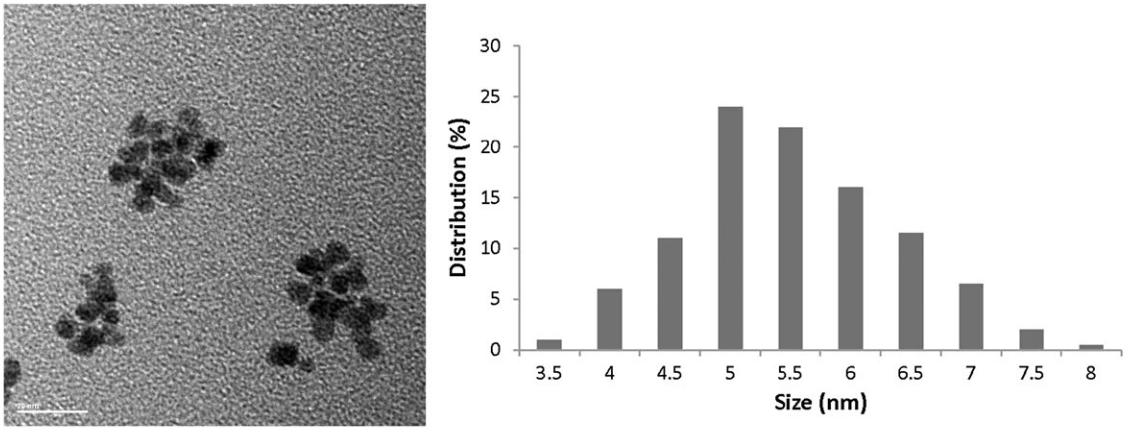


Fig. 3 TEM image and size distribution of palladium nanoparticles isolated from the Stille reaction between iodobenzene and tributylvinylstannane in **4b** (quenched after 15 minutes).

non-functionalized ILs, *e.g.* [emim][Tf_2N]. In binary mixtures, however, even those containing low concentrations of the functionalized ILs, recycling is possible with sustained catalytic activities observed comparable to that of the neat functionalized IL. However, recycling of Stille reactions led to a significant decrease in activity.

Conclusions

We have prepared a series of nitrile-functionalized pyrrolidinium ILs. The different chemical structures of the pyrrolidinium ILs compared to imidazolium and pyridinium-based ILs bearing the same nitrile functionality result in significantly different physical properties. All the ILs can be used as solvents for Suzuki and Stille C–C coupling reactions, and notably, the viscosity appears to influence the outcome of the reactions depending on the reaction mechanism, base activation in the Suzuki reaction *versus* transmetallation in the Stille reaction (see above). In both types of reactions nanoparticles have been isolated and the positive effect with respect to unfunctionalized ILs must, at least to some extent, be attributed to the ability of the nitrile group to favor nanoparticle-based processes. However, it is important to note that the nanoparticles are not considered to be the active catalytic species, but serve as reservoirs of Pd(0) from which the active catalyst is generated by oxidative addition of the aryl halide substrate. The nitrile group not only helps to stabilize the nanoparticles by weakly interacting with their surfaces, but also potentially stabilizes the active catalyst *via* coordination, with the combined stabilization effects preventing the formation of inactive (inaccessible) palladium black deposits. The ability to blend the functionalized ILs with other less expensive ILs is also attractive and further work is clearly needed to find the optimum IL mixtures that provide high reaction rates combined with high turnover numbers at lowest possible cost.

Experimental

1-Pyrrolidinebutanenitrile, iodomethane, iodoethane, iodopropane, iodobutane and lithium bis[(trifluoromethyl)sulfonyl]-imide, $LiTf_2N$ were obtained from commercial sources and used as received. The synthesis of the iodide salts **1a–4a** was performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques in dry solvents. ILs **1b–4b** were synthesized in water without precautions to exclude air. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 instrument. NMR spectra were measured on a Bruker DMX 400 using $SiMe_4$ as an external standard at 20 °C. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo-Finnigan LCQ™ Deca XP Plus quadrupole ion trap instrument on samples diluted in methanol according to a literature method.[38] Elemental analysis was carried out at the Institute of Chemical Sciences and Engineering (EPFL). Viscosities were measured with a Brookfield DV-II+ viscometer on 0.5 ml of sample. The temperature of the samples was maintained to 20 ± 1 °C by means of an external temperature controller. TEM images were obtained on a PHILIPS CM 20 transmission electron microscope. The size distribution is estimated from measuring 200 nanoparticles.

Synthesis of **1a**: methyl iodide (17.03 g, 0.12 mol) was added dropwise to a solution of 1-pyrrolidinebutanenitrile (13.82 g, 0.10 mol) in diethyl ether (50 ml) at 0 °C and the reaction mixture was stirred at RT for 24 h. The excess of methyl iodide and diethyl ether was then removed in vacuum. Yield: >99%. Mp 138 °C. ^{1}H-NMR (CD_2Cl_2): 3.70–3.97 (m, 6H), 3.27 (s, 3H), 2.80 (t, 2H, *J*(HH) = 7.0 Hz), 2.20–2.45 (m, 6H). IR (cm^{-1}): 2934, 2901, 2244, 1465, 1428, 1299, 1278, 1105, 1066, 998, 946, 906, 891, 728. ESI-MS (CH_3OH): positive ion: 153 [cation]. Anal. calc. for $C_9H_{17}IN_2$ (280.1474) C, 35.85; H, 6.12; N, 10.00%. Found: C, 36.00; H, 6.18; N, 10.02%.

Salts **2a–4a** were prepared using the same procedure as described for **1a**.

2a: yield: >99%. Mp 190 °C. ^{1}H-NMR (CD_2Cl_2): 3.30–3.60 (m, 6H), 2.45–2.70 (m, 4H), 2.10–2.25 (m, 4H), 1.70–1.90 (m, 2H), 1.31 (t, 3H, *J*(HH) = 7.0 Hz). IR (cm^{-1}): 2970, 2926, 2901, 2792, 2244, 1479, 1455, 1406, 1347, 1293, 1241, 1159, 1104, 1067, 1046, 1019, 998, 946, 929, 863, 808, 769, 734, 606. ESI-MS (CH_3OH): 167 [cation]. Anal. calc. for $C_{10}H_{19}IN_2$ (294.1743) C, 40.83; H, 6.51; N, 9.52%. Found: C, 41.00; H, 6.58; N, 9.50%.

3a: yield: >99%. Mp 142 °C. ^{1}H-NMR (CD_2Cl_2): 3.18–3.58 (m, 6H), 2.35–2.70 (m, 4H), 2.08–2.20 (m, 4H), 1.65–1.90 (m, 4H), 0.91 (t, 3H, *J*(HH) = 7.2 Hz). IR (cm^{-1}): 2969, 2901, 2248, 1458, 1408, 1379, 1231, 1065, 1049, 1003, 982, 940, 880, 819, 747, 634. ESI-MS (CH_3OH): 181 [cation]. Anal. calc. for $C_{11}H_{21}IN_2$ (308.2011) C, 42.87; H, 6.87; N, 9.09%. Found: C, 42.95; H, 6.91; N, 9.05%.

4a: yield: >99%. Mp 60 °C. ^{1}H-NMR (CD_2Cl_2): 3.20–3.60 (M, 6H), 2.50–2.70 (m, 4H), 2.10–2.15 (m, 4H), 1.65–1.90 (m, 4H), 1.35–1.45 (m, 2H), 0.93 (t, 3H, *J*(HH) = 7.4 Hz). IR (cm^{-1}): 2968, 2901, 2247, 1460, 1408, 1394, 1379, 1249, 1241, 1230, 1066, 1057, 906, 736, 632. ESI-MS (CH_3OH): 195 [cation]. Anal. calc. for $C_{12}H_{23}IN_2$ (322.2280) C, 44.73; H, 7.19; N, 8.69%. Found: C, 44.86; H, 7.21; N, 8.65%.

Synthesis of **1b**: $LiTf_2N$ (5.0 mmol) and **1a** (5.0 mmol) were dissolved in water (5 ml) forming immediately two phases. The phases were separated and the lower phase was washed with water (3 × 5 ml). The IL was dried in vacuum at 60 °C for 24 h. Yield: 69%. ^{1}H-NMR (CD_2Cl_2): 3.45–3.60 (m, 6H), 3.10 (s, 3H), 2.60 (t, 2H, *J*(HH) = 7.0 Hz), 2.15–2.40 (m, 6H), 1.70–1.85 (m, 2H), 1.30 (t, 3H, *J*(HH) = 7.0 Hz). IR (cm^{-1}): 2972, 2901, 2252, 1468, 1433, 1350, 1332, 1189, 1138, 1055, 891, 790, 762, 740, 631. ESI-MS (CH_3OH): positive ion: 153 [cation]. Anal. calc. for $C_{11}H_{17}F_6N_3O_4S_2$ (433.3961) C, 30.49; H, 3.95; N, 9.70%. Found: C, 30.51; H, 3.98; N, 9.74%.

ILs **2b–4b** were prepared using the same procedure as described for **1b**.

2b: yield: 71%. ^{1}H-NMR (CD_2Cl_2): 3.30–3.60 (m, 6H), 2.70–2.95 (m, 2H), 2.55 (t, 2H, *J*(HH) = 7.0 Hz), 1.95–2.55 (m, 6H), 1.38 (t, 3H, *J*(HH) = 7.0 Hz). IR (cm^{-1}): 2988, 2901, 2251, 1481, 1467, 1405, 1353, 1194, 1138, 1056, 891, 790, 740, 631. ESI-MS (CH_3OH): 167 [cation]. Anal. calc. for $C_{12}H_{19}F_6N_3O_4S_2$ (447.4230) C, 32.21; H, 4.28; N, 9.39%. Found: C, 32.31; H, 4.31; N, 9.34%.

3b: yield: 75%. ^{1}H-NMR (CD_2Cl_2): 3.15–3.60 (m, 6H), 2.56 (t, 2H, *J*(HH) = 7.0 Hz), 2.20–2.58 (m, 6H), 2.05–2.15 (m, 2H), 1.70–1.85 (m, 2H), 1.03 (t, 3H, *J*(HH) = 7.2 Hz). IR (cm^{-1}): 2979, 2889, 2251, 1480, 1467, 1349, 1331, 1187, 1137, 1054, 891, 789, 740, 631. ESI-MS (CH_3OH): 181 [cation]. Anal. calc. for $C_{13}H_{21}F_6N_3O_4S_2$ (461.4499) C, 33.84; H, 4.59; N, 9.11%. Found: C, 33.91; H, 4.61; N, 9.14%.

4b: yield: 68%. ^{1}H-NMR (CD_2Cl_2): 3.20–3.60 (M, 6H), 2.58 (t, 2H, *J*(HH) = 7.0 Hz), 2.10–2.45 (m, 8H), 1.65–1.75 (m, 2H), 1.38–1.48 (q, 2H, *J*(HH) = 7.4 Hz), 1.04 (t, 3H, *J*(HH) = 7.4 Hz). IR (cm^{-1}): 2971, 2901, 2253, 1467, 1352, 1193, 1138, 1056, 892, 789, 740, 631. ESI-MS (CH_3OH): 195 [cation]. Anal. calc. for $C_{14}H_{23}F_6N_3O_4S_2$ (475.4767) C, 35.37; H, 4.88; N, 8.84%. Found: C, 35.41; H, 4.91; N, 8.88%.

General catalytic Suzuki C–C coupling procedure

Reactions were performed in a 10 ml two-necked flask fitted with a septum and reflux condenser equipped with a gas-inlet adaptor. Aryl halide (0.5 mmol, 1 equiv.) and the ionic liquid (1.0 ml) were added, followed by phenylboronic acid (0.55 mmol, 1.1 equiv.), Na_2CO_3 (1.05 mmol, 2.1 equiv.) in water (0.5 ml), and finally the palladium chloride (0.006 mmol, 1.2 mol% based on aryl halide). The mixture was heated to 110 °C and stirred vigorously for 4 h. Subsequently the mixture was cooled to room temperature and extracted with diethyl ether (3 × 5 ml). The combined extracts were washed with brine and water and then dried with $MgSO_4$. The biphenyl product was obtained following filtration and removal of the solvent under vacuum. The products were analyzed by GC.

General catalytic Stille C–C coupling procedure

Reactions were performed in a 10 ml two-necked flask fitted with a septum and reflux condenser equipped with a gas-inlet adaptor. Aryl halide (0.5 mmol, 1 equiv.) and the ionic liquid (1.0 ml) were added, followed by tributylvinylstannane (0.6 mmol, 1.2 equiv.), and finally the palladium chloride (0.025 mmol, 5 mol% based on aryl halide). The mixture was heated to 80 °C and stirred vigorously for 4 h. Subsequently the mixture was cooled to room temperature and extracted with diethyl ether (3 × 5 ml). The combined extracts were washed with brine and water and then dried with $MgSO_4$. The styrene products were analyzed by GC.

Catalyst recycling: after catalysis and product extraction (see above) the IL-palladium solution was washed with water (2 × 1 ml) and dried under vacuum for 18 h and then charged with further substrates and reacted (as described above).

Preparation of palladium nanoparticles

$PdCl_2$ (15 mg) was dissolved in **1b** (2 ml) or **4b** (2 ml) and heated to 110 °C for 1 h. The reaction mixture was cooled to room temperature and $NaBH_4$ (5 mg) in water (0.2 ml) was added. A black suspension immediately formed. After stirring at room temperature for 4 h, the reaction mixture was washed with water (2 × 0.5 ml) and dried under vacuum.

Preparation of TEM samples

A sample (0.1 ml) from the Suzuki coupling reaction in **1b** (or a sample of 0.1 ml from the Stille reaction in **4b**) was diluted in 2.0 ml of ethanol and the solution was ultrasonicated for 30 min at room temperature. One drop of this solution was then deposited on a carbon film copper grid (200 mesh) and dried under vacuum overnight.

Crystallography†

Data collection for the X-ray structure determination was performed on a KUMA CCD diffractometer system using graphite-monochromated MoKα radiation and a low-temperature device [*T* 140(2) K]. Crystals suitable for X-ray

Table 5 Crystal data and structure refinement for **1a**

Identification code	pd344	
Empirical formula	$C_9H_{17}IN_2$	
Formula weight	280.15	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	a = 13.0165(5) Å	α = 90°
	b = 9.4458(5) Å	β = 90°
	c = 18.5173(7) Å	γ = 90°
Volume	2276.73(17) Å^3	
Z	8	
Density (calculated)	1.635 Mg m^{-3}	
Absorption coefficient	2.770 mm^{-1}	
F(000)	1104	
Crystal size	0.37 × 0.26 × 0.19 mm	
θ range for data collection	2.70 to 25.01°	
Index ranges	$-15 \le h \le 15, -10 \le k \le 10, -22 \le l \le 22$	
Reflections collected	13 021	
Independent reflections	1991 [*R*(int) = 0.0382]	
Completeness to θ = 25.01°	99.2%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.51222	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1991/0/109	
Goodness-of-fit on F^2	1.135	
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0302, wR_2 = 0.0641	
R indices (all data)	R_1 = 0.0409, wR_2 = 0.0719	
Largest diff. peak and hole	0.664 and −0.711 e Å^{-3}	

diffraction studies were obtained from slow diffusion of diethyl ether into an acetonitrile solution. Data reduction was performed using CrysAlis RED,[39] and structure solution and refinement were carried out using the SHELX97 software package.[40] The structure was solved by Patterson methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). All non-hydrogen atoms were refined anisotropically, and the contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Relevant crystallographic data are compiled in Table 5.

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References

1 (*a*) K. R. Seddon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 351; (*b*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (*c*) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; (*d*) P. J. Dyson, *Appl. Organomet. Chem.*, 2002, **16**, 495; (*e*) J. Dupont, R. F. D. Souza and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667; (*f*) C. Ciappe and D. Pieraccini, *J. Phys. Org. Chem.*, 2005, **18**, 275; (*g*) P. Migowski and J. Dupont, *Chem.–Eur. J.*, 2007, **13**, 32.

2 A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis, Jr. and R. D. Rogers, *Chem. Commun.*, 2001, 135.

3 J. H. Davis, Jr., *Chem. Lett.*, 2004, **33**, 1072.

4 Z. Fei, T. J. Geldbach, D. Zhao and P. J. Dyson, *Chem.–Eur. J.*, 2006, **12**, 2122.

5 (*a*) H. Xue, B. Twamley and J. M. Shreeve, *J. Org. Chem.*, 2004, **69**, 1397; (*b*) B. A. Omotowa and J. M. Shreeve, *Organometallics*, 2004, **23**, 783; (*c*) B. A. Omotowa, B. S. Phillips, J. S. Zabinski and J. M. Shreeve, *Inorg. Chem.*, 2004, **43**, 5466; (*d*) O. D. Gupta, P. D. Armstrong and J. M. Shreeve, *Tetrahedron Lett.*, 2003, **44**, 9367; (*e*) Y. Gao, S. W. Arritt, B. Twamley and J. M. Shreeve, *Inorg. Chem.*, 2005, **44**, 1704; (*f*) J.-C. Xiao, C. Ye and J. M. Shreeve, *Org. Lett.*, 2005, **7**, 1963.

6 D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti and P. J. Dyson, *J. Am. Chem. Soc.*, 2004, **126**, 15876.

7 (*a*) J. Ropponen, M. Lahtinen, S. Busi, M. Nissinen, E. Kolehmainen and K. Rissanen, *New J. Chem.*, 2004, **28**, 1426; (*b*) B. Martiz, R. Keyrouz, S. Gmouh, M. Vaultier and V. Jouikov, *Chem. Commun.*, 2004, 674.

8 For example see: (*a*) C. Daguenet and P. J. Dyson, *Organometallics*, 2004, **23**, 6080; (*b*) P. Illner, A. Zahl, R. Puchta, H. N. van Eikema, P. Wasserscheid and R. van Eldik, *J. Organomet. Chem.*, 2005, **690**, 3567; (*c*) C. Daguenet and P. J. Dyson, *Organometallics*, 2006, **25**, 5811; (*d*) P. Illner, S. Begel, S. Kern, R. Puchta and R. van Eldik, *Inorg. Chem.*, 2009, **48**, 588.

9 (*a*) C. J. Mathews, P. J. Smith and T. Welton, *Chem. Commun.*, 2000, 1249; (*b*) F. Fernández, B. Cordero, J. Durand, G. Muller, F. Malbosc, Y. Kihn, E. Teuma and M. Gómez, *Dalton Trans.*, 2007, 5572; (*c*) J. Duranda, E. Teumaa, F. Malboscb, Y. Kihnc and M. Gómez, *Catal. Commun.*, 2008, **9**, 273; (*d*) V. Calò, A. Nacci, A. Monopoli and F. Montingelli, *J. Org. Chem.*, 2005, **70**, 6040.

10 B. F. G. Johnson, *Top. Catal.*, 2003, **24**, 147.

11 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.

12 J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508.

13 (*a*) G. P. Wolfe, R. A. Singer, B. H. Yang and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 9550; (*b*) G. Matsuo and S. Matsumura, *Tetrahedron Lett.*, 2001, **42**, 7375; (*c*) A. H. M. de Vries and J. G. de Vries, *Adv. Synth. Catal.*, 2004, **346**, 1812.

14 C. Chiappe, D. Pieraccini, D. Zhao, Z. Fei and P. J. Dyson, *Adv. Synth. Catal.*, 2006, **348**, 68.

15 D. Zhao, Z. Fei, R. Scopelliti and P. J. Dyson, *Inorg. Chem.*, 2004, **43**, 2197.

16 S. R. Dubbaka, D. Zhao, Z. Fei, C. M. Rao Volla, P. J. Dyson and P. Vogel, *Synlett*, 2006, 3155.

17 X. Yang, Z. Fei, D. Zhao, W. H. Ang, Y. Li and P. J. Dyson, *Inorg. Chem.*, 2008, **47**, 3292.

18 F. Mazille, Z. Fei, D. Kuang, D. Zhao, S. M. Zakeeruddin, M. Graetzel and P. J. Dyson, *Inorg. Chem.*, 2006, **45**, 1585.

19 P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2003.

20 C. J. Mathews, P. J. Smith, T. Welton, A. J. P. White and D. J. Williams, *Organometallics*, 2001, **20**, 3848.

21 J. McNulty, A. Capretta, J. Wilson, J. Dyck, G. Adjabeng and A. Robertson, *Chem. Commun.*, 2002, 1986.

22 M. Lombardo, M. Chiarucci and C. Trombini, *Green Chem.*, 2009, **11**, 574.

23 G. Zou, Z. Wang, J. Zhu, J. Tang and M. Y. He, *J. Mol. Catal. A: Chem.*, 2003, **206**, 193.

24 X. Yang, Z. Fei, T. J. Geldbach, A. D. Phillips, C. G. Hartinger, Y. Li and P. J. Dyson, *Organometallics*, 2008, **27**, 3971.

25 C. Chiappe, *Monatsh. Chem.*, 2007, **138**, 1035.

26 C. F. Poole, *J. Chromatogr., A*, 2004, **1037**, 49.

27 C. C. Cassol, A. P. Umpierre, G. Machado, S. I. Wolke and J. Dupont, *J. Am. Chem. Soc.*, 2005, **127**, 3298.

28 (*a*) C. W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtner and S. R. Texeira, *Inorg. Chem.*, 2003, **42**, 4738; (*b*) J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner and S. R. Teixeira, *J. Am. Chem. Soc.*, 2002, **124**, 4228.

29 V. Calo, A. Nacci, A. Monopoli, S. Laera and N. Cioffi, *J. Org. Chem.*, 2003, **68**, 2929.

30 X.-D. Mu, D. G. Evans and Y. Kou, *Catal. Lett.*, 2004, **97**, 151.

31 J. Durand, E. Teuma, F. Malbosc, Y. Kihn and M. Gómez, *Catal. Commun.*, 2008, **9**, 273.

32 R. R. Deshmukh, R. Rajagopal and K. V. Srinivasan, *Chem. Commun.*, 2001, 1544.

33 D.-J. Guo and H.-L. Li, *J. Colloid Interface Sci.*, 2005, **286**, 274.

34 Z. Fei, D. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe and P. J. Dyson, *Organometallics*, 2007, **26**, 1588.

35 Y. Umebayashi, S. Fukuda, Y. Kameda and S. Kohara, *Research Frontiers*, 2007, 118.

36 R. Bini, O. Bortolini, C. Chiappe, D. Pieraccini and T. Siciliano, *J. Phys. Chem. B*, 2007, **111**, 598.

37 (*a*) M. T. Barros, C. D. Maycock, M. I. Madureira and M. R. Ventura, *Chem. Commun.*, 2001, 1662; (*b*) V. Farina and E. Napolitano, *Organometallics*, 2003, **22**, 4030.

38 P. J. Dyson and J. S. McIndoe, *Inorg. Chim. Acta*, 2003, **354**, 68.

39 Oxford Diffraction Ltd., M.P., Abingdon OX14 4 RX, UK, 2007.

40 G. M. Sheldrick, *SHELX-97, Structure Solution and Refinement Package*, Universitaet Goettingen, Goettingen, Germany, 1997.