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Evaluation of ionic liquid soluble imidazolium tetrachloropalladate pre-catalysts in Suzuki coupling reactions

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ABSTRACT

Imidazolium salts with aromatic groups 1,3-bis(9-anthracenylmethyl)imidazolium chloride ([Bamim]Cl), 1,3-bis(1-naphthalenylmethyl)imidazolium chloride ([Bnmim]Cl) and 1,3-bis(benzylmethyl)imidazolium chloride ([Bbmim]Cl) were reacted with $PdCl_2$ forming the analogous tetrachloropalladate salts. These palladium-containing salts were evaluated as pre-catalysts in Suzuki cross-coupling reactions in ionic liquids generally resulting in high conversions. The formation of palladium nanoparticles is observed and their role in the overall catalytic mechanism is discussed.

1. Introduction

The Suzuki C—C cross-coupling reaction is a convenient way to generate C—C bonds via the coupling aryl halides with arylboronic acids in the presence of a palladium catalyst. Since its discovery, this reaction has emerged as an extremely efficient and important tool in organic synthesis, and is used in a variety of industrial processes [1–3]. Despite the utility of the reaction, contamination of the products with palladium residues, recovery and reuse of the catalysts, and the use of organic solvents can be problematic. Some heterogeneous Pd-catalyzed Suzuki coupling systems have been described in recent years, such as Pd—C [4–9], mesoporous zeolites [10], polymer supported Pd-catalysts [11–15] and Pd nanoparticles (NPs) [16–21]. These systems offer advantages over the homogeneous catalytic systems as product purification and catalyst recycling are relatively facile.

Ionic liquids are interesting solvents in which to conduct Suzuki reactions with simple palladium salts under 'ligand-free' conditions offering a compromise between homogeneous and heterogeneous catalytic conditions [2,22–28]. We have previously reported imidazolium and pyridinium-based ILs with nitrile functionalities attached to the alkyl side that serve as both solvents and stabilizers for palladium NPs reservoirs used in carbon–carbon coupling reactions [19,24]. The nitrile group appears to stabilize the NPs by interactions with the palladium surface and simultaneously helps to stabilize the active mononuclear palladium(II) catalyst generated in situ by coordination, and combined these stabilization effects prevent the formation of palladium black.

In this work, the imidazolium-based salts 1,3-bis(9-anthracenylmethyl)imidazolium chloride ([Bamim][Cl]), 1,3-bis(1-naphthalenylmethyl)imidazolium chloride ([Bnmim][Cl]), 1,3-bis(benzylmethyl)imidazolium chloride ([Bbmim][Cl]), which contain bulky peripheral groups were prepared. These salts were subsequently converted to tetrachloropalladate salts and evaluated as pre-catalysts in Suzuki coupling reactions performed in 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, [Emim][Tf_2N], allowing the influence of the substituent on the cation to be assessed.

2. Experimental

2.1. Chemicals and instrumentation

[Bbmim][Cl] [29] and [Bamim][Cl] [30] were prepared according to literature methods. All other reagents were obtained from Aldrich except for Li[Tf_2N] which was purchased from Iolitec

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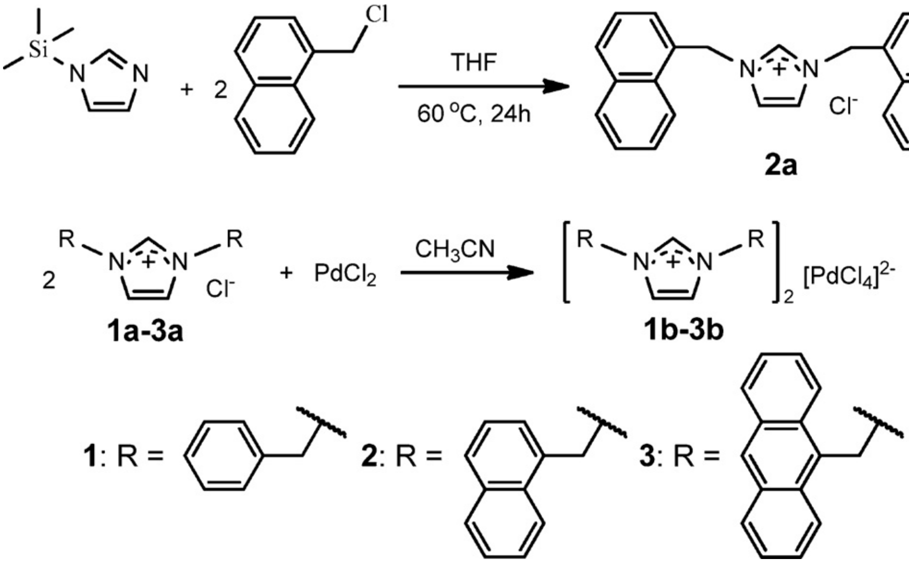
Table 1
Crystal data and structural refinement parameters for **1b**, **2b** and **3b**.

	1b	**2b**	**3b·1/4Et$_2$O**
CCDC depository	846916	846917	846918
Formula	$C_{34}H_{34}N_4Cl_4Pd$	$C_{50}H_{42}N_4Cl_4Pd$	$C_{67}H_{52.5}N_4O_{0.25}Cl_4Pd$
Formula weight	746.85	947.08	1165.83
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.8349(7)	9.7281(7)	16.079(3)
b (Å)	8.7778(15)	15.448(3)	18.392(4)
c (Å)	16.394(2)	15.890(3)	20.551(4)
α (°)	90	116.140(13)	80.234(15)
β (°)	107.086(8)	90.320(11)	89.443(15)
γ (°)	90	98.243(10)	65.142(15)
V (Å^3)	1627.9(4)	2115.1(6)	5421.6(19)
Z	2	2	4
Crystal size (mm)	0.43 × 0.36 × 0.25	0.47 × 0.18 × 0.12	0.24 × 0.24 × 0.11
ρ (g cm^{-1})	1.524	1.487	1.428
μ (mm^{-1})	0.929	0.733	0.587
Reflections collected	69,132	39,012	60,229
Independent reflections (R_{int})	10,047(0.0249)	9649(0.0596)	18,763(0.0830)
Data/restraints/parameters	10,047/0/196	9649/0/532	18,763/0/1400
Goodness of fit of F^2	1.172	1.148	1.604
Final indexes [$I > 2\sigma(I)$]	$R_1 = 0.0210$	$R_1 = 0.0589$	$R_1 = 0.1348$
	$wR_2 = 0.0507$	$wR_2 = 0.1370$	$wR_2 = 0.3708$
Final indexes (all data)	$R_1 = 0.0320$	$R_1 = 0.0797$	$R_1 = 0.1975$
	$wR_2 = 0.0587$	$wR_2 = 0.1492$	$wR_2 = 0.4264$
Largest difference (e Å^{-3})	0.672 and −1.144	3.690 and −0.829	6.239 and −2.252

(Germany), and used as received. Solvents were dried using appropriate reagents and distilled prior to use. Compounds were synthesized under an inert atmosphere of dry nitrogen using standard Schlenk techniques. NMR spectra were recorded at 25 °C on a Bruker 400 DMX Spectrometer using Me_4Si as an external standard. Electrospray ionization mass spectroscopy (ESI-MS) was performed on a Q-Tof Ultima mass spectrometer (Waters) operated in positive ionization mode and fitted with a standard Z-spray ion source equipped with a Lock-Spray interface. The sample was diluted in acidified CH_3OH (∼5–10 M) and 5 ml was introduced into the mass spectrometer by infusion at a flow rate of 20 ml/min with a solution of CH_3OH. Experimental parameters were set as follows: capillary voltage: 3.5 kV, sample cone: 35 V, source temperature: 80 °C, desolvation temperature: 200 °C, acquisition window: m/z 100–1000 in 1 s. External calibration was carried out with a solution of phosphoric acid at 0.01% introduced through an orthogonal ES probe. Data from the Lock-Spray are used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. Transmission electron microscopy (TEM) was carried out on a Hitachi H-9000 electron microscope operated at 300 kV. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. Elemental analysis was carried out at the EPFL. GC analysis was carried out on a Varian Chrompack CP-3380 equipped with a capillary column (25 m × 0.25 mm, using N_2 as carrier gas).

2.2. Synthesis

Preparation of [Bnmim][Cl] **2a**: A mixture of trimethylsilylimidazole (14.03 g, 0.1 mol) and 1-(chloromethyl)naphthalene



Scheme 1. Synthesis of [Bnmim][Cl] **2a**, [(Bbmim)$_2$][PdCl$_4$] **1b**, [(Bnmim)$_2$][PdCl$_4$] **2b** and [(Bamim)$_2$][PdCl$_4$] **3b**.

(37.09 g, 0.21 mol) in THF (50 ml) was heated at 60 °C for 24 h. The resulting solid was collected by filtration and washed with diethyl ether (3× 20 ml) and dried under vacuum for 24 h. Yield: 35.8 g, 93%. M.p. 208.8 °C. ^{1}H NMR (400 MHz, d_4-CD$_3$OD,): δ = 9.1 (s, 1H), 8.0 (t, 4H, J = 8 Hz), 7.9 (d, 2H, J = 8 Hz), 7.5–7.6 (m, 10H), 5.90 (s, 4H). ^{13}C NMR (100.5 MHz, d_4-CD$_3$OD): δ = 136.2, 134.1, 130.7, 130.2, 128.9, 128.6, 128.3, 127.1, 126.2, 125.2, 122.6, 121.9, 50.8. HRESI-MS (H_2O) m/z: 349.1705 ([Bnmim]$^+$, calc. for $C_{25}H_{21}N_2$ 349.1705). FTIR: ν (cm^{-1}) 3124 (C—H aromatic), 3074 (C—H aromatic), 2984 (C—H alkyl), 1618 (C=C aromatic). Anal. Calc. for $C_{25}H_{21}N_2Cl$ (384.90) C, 78.01; H, 5.50; N, 7.28%. Found: C, 77.89; H, 5.56; N, 7.26%.

Preparation of [(Bbmim)$_2$][PdCl$_4$] **1b**: [Bbmim]Cl (570 mg, 2 mmol) was added to a Schlenk tube containing acetonitrile (5 ml). $PdCl_2$ (177 mg, 1 mmol) was then added and the solution stirred vigorously at room temperature for 12 h. After removal of the solvent, the resulting orange solid was collected by centrifugation, washed with dichloromethane (2× 5 ml), and dried under vacuum to give **1b**. Yield: 684 mg, 92%. M.p. 180.7 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.3 (s, 1H), 7.6 (s, 2H), 7.4 (m, 10H), 5.4 (s, 4H). ^{13}C NMR (100.5 MHz, d_6-DMSO): δ = 136.7, 135.2, 129.5, 129.2, 128.8, 123.3, 52.5. HRESI-MS (H_2O) m/z: 249.1392 ([Bbmim]$^+$, calc. for $C_{17}H_{17}N_2$ 249.1392). FTIR: ν (cm^{-1}) 3137 (C—H aromatic), 3029 (C—H aromatic), 1619 (C=C aromatic). Anal. Calc. for $C_{34}H_{34}N_4Cl_4Pd$ (746.89) C, 54.68; H, 4.59; N, 7.50%. Found: C, 54.49; H, 4.65; N, 7.46%.

Preparation of [(Bnmim)$_2$][PdCl$_4$] **2b**: [Bnmim]Cl (770 mg, 2 mmol) was added to a Schlenk tube containing acetonitrile (5 ml). $PdCl_2$ (177 mg, 1 mmol) was added and the solution stirred vigorously at room temperature for 12 h. After removal of the solvent, the resulting orange solid was collected by centrifugation, washed with dichloromethane (2× 5 ml), and dried under vacuum to afford **2b**. Yield: 852 mg, 90%. M.p. 236.7 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.4 (s, 1H), 8.0–8.1 (m, 6H), 7.80 (s, 2H), 7.5–7.6 (m, 8H), 5.9 (s, 4H). ^{13}C NMR (100.5 MHz, d_6-DMSO): δ = 137.2, 133.9, 130.8, 130.4, 130.2, 129.4, 128.1, 127.6, 126.9, 126.0, 123.5, 123.2, 50.5. HRESI-MS (H_2O) m/z: 349.1705 ([Bnmim]$^+$, calc for $C_{25}H_{21}N_2$ 349.1705). FTIR: ν (cm^{-1}) 3137 (C—H aromatic), 3029 (C—H aromatic), 1619 (C=C aromatic). Anal. Calc. for $C_{50}H_{42}N_4Cl_4Pd$ (947.13) C, 63.41; H, 4.47; N, 5.92%. Found: C, 63.29; H, 4.55; N, 5.87%.

Preparation of [(Bamim)$_2$][PdCl$_4$] **3b**: [Bamim]Cl (970 mg, 2 mmol) was added to a Schlenk tube containing acetonitrile (5 ml), $PdCl_2$ (177 mg, 0.5 mmol) was added and the solution stirred vigorously at room temperature for 12 h. After removal of the solvent, the resulting orange solid was collected by centrifugation, washed with dichloromethane (2× 5 ml), and dried under vacuum to give the product **3b**. Yield: 1043 mg, 91%. M.p. 247.6 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.1 (s, 1H), 8.8 (s, 2H), 8.3 (d, 4H, J = 8.0 Hz), 8.2 (d, 4H, J = 8.0 Hz), 7.6 (t, 8H, J = 4.0 Hz), 7.2 (s, 2H), 6.4 (s, 4H). ^{13}C NMR (100.5 MHz, d_6-DMSO): δ = 136.0, 131.4, 130.9, 130.6, 129.8, 128.2, 126.0, 123.8, 123.5, 122.7, 45.2. HRESI-MS (H_2O) m/z: 449.2018 ([Bamim]$^+$, calc for $C_{33}H_{25}N_2$ 449.2018). FTIR: ν (cm^{-1}) 3118 (C—H aromatic), 3040 (C—H aromatic), 1622 (C=C aromatic). Anal. Calc. for $C_{66}H_{50}N_4Cl_4Pd$ (1147.36) C, 69.09; H, 4.39; N, 4.88%. Found: C, 68.91; H, 4.45; N, 4.86%.

2.3. General procedure for the Suzuki reactions

To a 10 ml flask fitted with a reflux condenser, aryl halide (0.5 mmol, 1 equiv), catalyst **3b** (1.0 mol% based on aryl halide), [Emim][Tf$_2$N] (1.0 ml), phenylboronic acid (0.55 mmol, 1.1 equiv), Na_2CO_3 (112 mg, 1.05 mmol, 2.1 equiv), and water (0.5 ml) were added. The mixture was heated to 100 °C and stirred vigorously. After reaction, the mixture was cooled and the products were extracted with diethyl ether (3× 5 ml). The combined extracts were dried with Na_2SO_4 overnight, filtered and analyzed by GC.

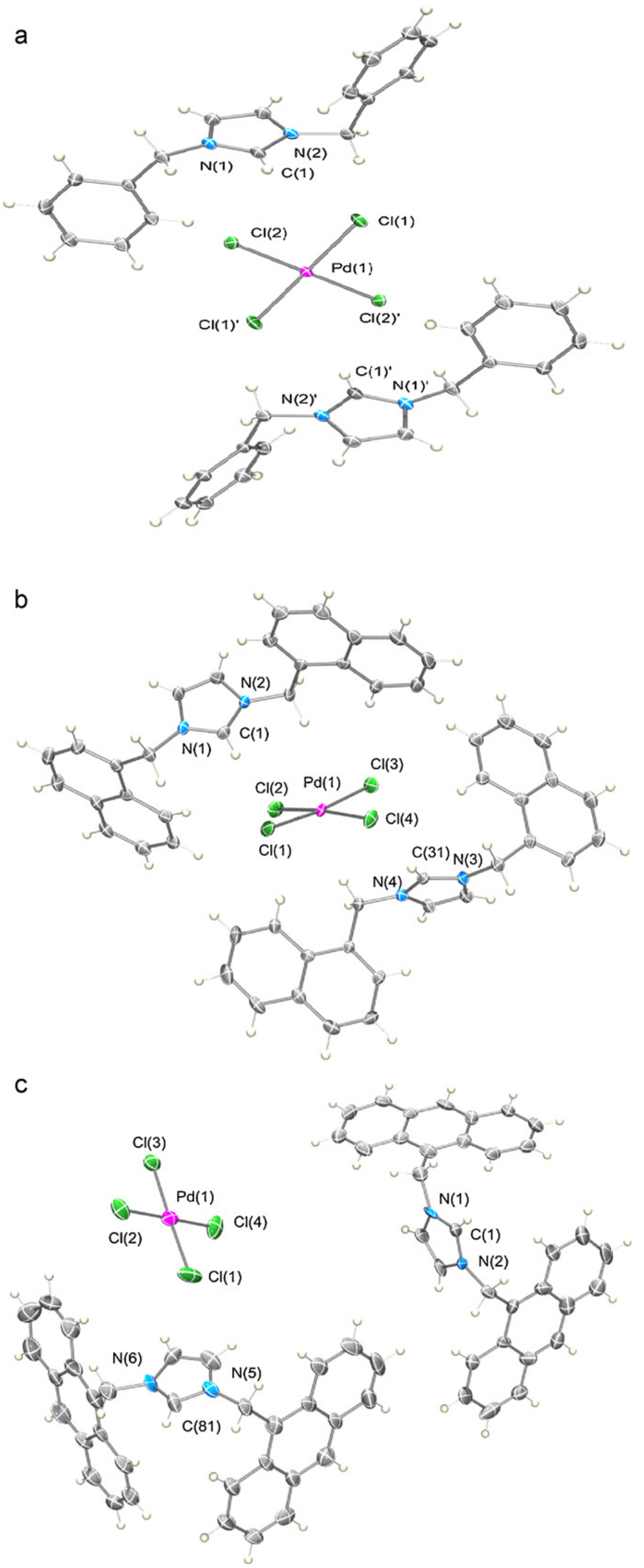
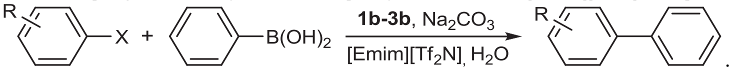


Fig. 1. Molecular structures of (a) **1b**, (b) **2b** and (c) **3b**. Selected bond distances (Å) and angles (°). **1b**: C(1)–N(1) 1.3332(12), C(1)–N(2) 1.3371(11), Pd(1)–Cl(1) 2.3085(5), Pd(1)–Cl(2) 2.3248(4); N(1)–C(1)–N(2) 108.38(8). **2b**: C(1)–N(1) 1.332(5), C(1)–N(2) 1.336(5), C(31)–N(3) 1.334(5), C(31)–N(4) 1.341(5), Pd(1)–Cl(1) 2.3002(9), Pd(1)–Cl(2) 2.3062(9); N(1)–C(1)–N(2) 109.4(2); **3b**: C(1)–N(1) 1.333(2), C(1)–N(2) 1.358(2), Pd(1)–Cl(1) 2.337(6), Pd(1)–Cl(2) 2.333(5); N(1)–C(1)–N(2) 117.7(14) (Et_2O solvate omitted for clarity).

Table 2
Suzuki coupling between aryl halides and phenylboronic acid in [Emim][Tf_2N] with pre-catalysts **1b**–**3b**.



Entry	R	Aryl halide	Pre-catalyst	Yield (%)[a]
1	2-Me	X = Br	**1b**	83
2	2-Me	X = Br	**2b**	83
3	2-Me	X = Br	**3b**	90
4	2-Me	X = I	**1b**	65
5	2-Me	X = I	**2b**	73
6	2-Me	X = I	**3b**	82
7	4-OMe	X = Br	**1b**	97
8	4-OMe	X = Br	**2b**	98
9	4-OMe	X = Br	**3b**	99
10	4-OMe	X = I	**1b**	98
11	4-OMe	X = I	**2b**	98
12	4-OMe	X = I	**3b**	98
13	4-NO_2	X = Br	**1b**	99
14	4-NO_2	X = Br	**2b**	99
15	4-NO_2	X = Br	**3b**	99
16	4-NO_2	X = I	**1b**	99
17	4-NO_2	X = I	**2b**	99
18	4-NO_2	X = I	**3b**	99

Conditions: The appropriate aryl halide (0.5 mmol), phenylboronic acid (0.55 mmol), Na_2CO_3 (1.05 mmol in 0.5 ml H_2O) and the pre-catalyst **1b**, **2b** or **3b** (0.006 mmol) in [Emim][Tf_2N] (1.0 ml) was heated at 100 °C for 4 h.

[a] Yields of corresponding products were determined by GC.

2.4. Preparation of TEM samples

A sample (0.1 ml) from the Suzuki coupling reaction (entry 1 in Table 3) was diluted in ethanol (2.0 ml) 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 meshes) and dried under vacuum for 18 h.

2.5. X-ray data collection and refinement

X-ray data for **1b**, **2b** and **3b** were recorded on an APEX II CCD diffractometer at 100 K using Mo-Kα radiation (λ = 0.71073 Å). Absorption corrections were applied by semi-empirical methods [31]. The structures were solved using SHELX and weighted full-matrix least-squares refinement on F2 was carried out using SHELXL-97 [32], with all non-hydrogen atoms being refined anisotropically. The hydrogen atoms were included in calculated positions and were refined as riding atoms with individual (or if appropriate group) isotropic displacement parameters. All ORTEP [33] diagrams have been drawn with 50% probability ellipsoids. Crystal data and collection parameters are given in Table 1. CCDC 846916–846918 contains the supplementary crystallographic data for these structures. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

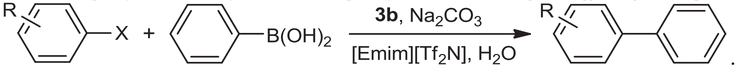
3. Results and discussion

3.1. Synthesis and characterization of the imidazolium salts

[Bnmim][Cl] **2a**, [$(Bbmim)_2$][$PdCl_4$] **1b**, [$(Bnmim)_2$][$PdCl_4$] **2b**, and [$(Bamim)_2$][$PdCl_4$] **3b** are new compounds and their synthesis is outlined in Scheme 1. Reaction of the chloride salts **1a**–**3a** with $PdCl_2$ in a 2:1 molar ratio in acetonitrile leads to the formation of the tetrachloropalladates **1b**–**3b**, as reported previously for related salts [34]. Salts **1b**–**3b** are air-stable and insoluble in non-polar or low-polarity solvents such as diethyl ether and THF, **1b** and **2b** are slightly soluble in dichloromethane, chloroform and highly soluble in acetonitrile. Salt **3b** is only soluble in dimethylformide (DMF) and dimethylsulfoxide (DMSO). Spectroscopic data for **1b**–**3b** are essentially routine (see Section 2), however, single crystals of the salts were obtained and their structures were determined by X-ray diffraction so that the structural variations within series could be ascertained. **3b** shows signs of twinning (see Section 2.5) and as a result refinement was poor although the connectivity could be established.

The structures of **1b**, **2b** and **3b** are presented in Fig. 1 with selected bond lengths given in the caption. The two substituents attached to the imidazolium cation ring are *trans* along the planar five-membered ring in **1b** and **2b**. In **3b**, the two anthracene rings are located at the same side of the imidazolium ring, forming a

Table 3
Suzuki coupling between aryl halides and phenylboronic acid in [Emim][Tf_2N] in the presence of **3b**.



Entry	R	Aryl halide	Yield (%)[a]
1	H	X = Br	88
2	H	X = I	93
3	4-Me	X = I	99
4	4-OMe	X = I	98
5	2-CN	X = Br	99

Conditions: The aryl halide (0.5 mmol), phenylboronic acid (0.55 mmol), Na_2CO_3 (1.05 mmol in 0.5 ml H_2O) and catalyst **3b** (0.006 mmol) in ionic liquid (1.0 ml) was heated at 100 °C for 4 h.

[a] Yields of corresponding products were determined by GC.

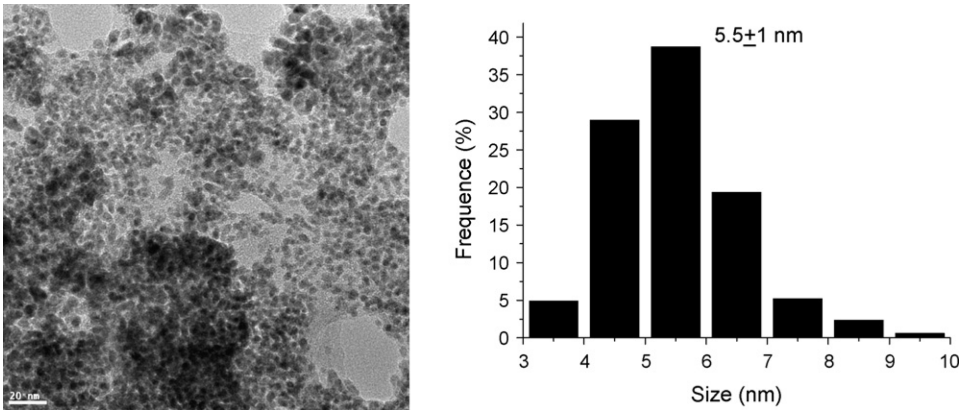


Fig. 2. TEM image and size distribution of palladium nanoparticles generated in the Suzuki reaction between bromobenzene and phenylboronic acid using pre-catalyst **3b**.

butterfly structure with the two bulky anthracene groups embracing the $[PdCl_4]^{2-}$ anion.

The bond parameters within the anions in the salts of **1b**–**3b** are very similar and in all cases the $[PdCl_4]^{2-}$ anion is essentially square-planar with the Pd—Cl distances ranging from 2.300 Å in **2b** to 2.326 Å in **3b**. The bonding in the cations of **1b**, **2b** and **3b** are comparable to other imidazolium salts with the $[PdCl_4]^{2-}$ anion [34]. Notably, the N—C—N angle increases gradually from 108.38° in **1b** to 109.39° in **2b** and to 110.32° in **3b**. The N—N distances within the imidazolium cation increases slightly from 2.166 Å in **1b** to 2.168 Å in **2b** and to 2.183 Å in **3b**. Nevertheless, the bond lengths in the imidazolium cation of **1b** are comparable to those that have been characterized previously [29,35] in other salts.

3.2. *Catalytic activity of* ***1b*–*3b*** *in Suzuki reactions*

Suzuki C—C coupling reactions between phenylboronic acid and arylhalides were studied in $[Emim][Tf_2N]$ using **1b**–**3b** as pre-catalysts (see Table 2). It appears that the peripheral substituents on the imidazolium cations influence catalytic activity, with the most sterically encumbered salt, 1,3-bis(9-anthracenylmethyl)imidazolium, giving the highest conversions. These differences are not easily rationalized but can probably be traced to the mechanism by which the system catalyzes the reaction. Based on other studies the mechanism is believed to involve the initial reduction of the Pd(II) ions in the tetrachloropalladate pre-catalysts to form Pd(0) nanoparticles (see below), which are subsequently oxidized to a Pd(II) species following oxidative addition of the aryl halide substrate [21,26,36,37]. In the tetrachloropalladate catalytic system described herein the catalytic reaction media gradual darken in color and following reaction palladium nanoparticles were extracted and analyzed by TEM (see below).

Based on the proposed mechanism and the observation of nanoparticles in the reaction medium it is not unreasonable to assume that the anthracene-substituents interact most effectively with the nanoparticles which leads to the higher catalytic activity with pre-catalyst **3b**. Indeed, excellent catalytic activity of palladium nanoparticle–graphene hybrid catalysts in which the graphene sheets stabilize the Pd nanoparticles against aggregation have been reported [38], and are late defect may be provided by the cation in **3b**. An analysis of the packing in **3b** reveals the presence of cavities (ca. 1 nm^3) formed from the faces of the anthracenyl substituents. In the solid state these cavities contain disordered diethyl ether solvent, however it is not unreasonable to speculate that these supramolecular forces are retained in the ionic liquid, and in a manner similar to graphene, act to stabilize the nanoparticles. Notably, these cavities are absent in the both **1b** and **2b**. TEM

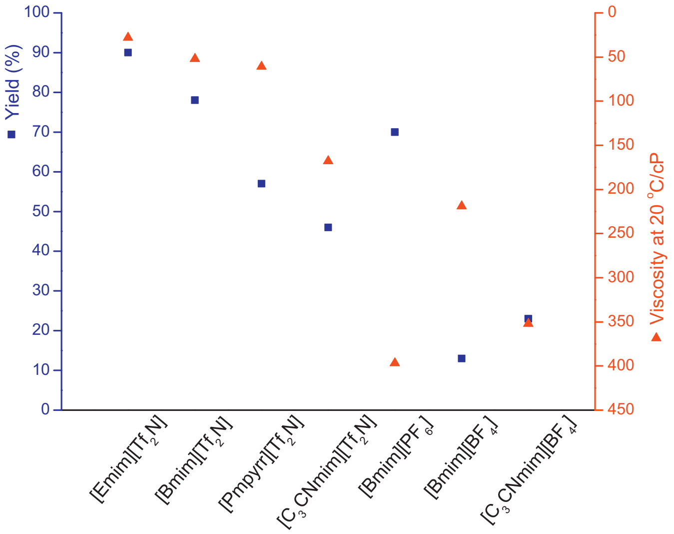


Fig. 3. Yields of the coupling product with respect to the viscosities of the neat ILs.

of the Pd nanoparticles isolated from the reaction employing **3b** as the pre-catalyst reveals the formation of particles with a size distribution centered around 5.5 nm (Fig. 2).

The scope of the reaction with using **3b** as the pre-catalyst was expanded with a range of substituted aryl bromides with varying electronic and/or steric properties (Table 3). The reaction proceeds well with aryl halides containing electron-donating groups, such as 4-methyliodobenzene and 4-methoxyiodobenzene (Table 3, entries 3 and 4), and aryl halides with an electron-withdrawing nitrile group afforded the coupling products almost quantitatively (Table 3, entry 5).

Besides the effects of the catalysts and substrates, the viscosities of the ILs possibly play a role by influencing mass transfer. For example, reaction in $[Emim][Tf_2N]$ (yield 90%) is more efficient than in $[Bmim][Tf_2N]$ (78%), which could be ascribed to a viscosity difference (28 cP vs. 52 cP [39]). Furthermore, the reaction is very slow in $[C_3CNmim][BF_4]$ which has the highest viscosity (352 cP [40]). The yield of coupling product indeed exhibits some relationship with IL viscosity (Fig. 3), i.e. the higher the viscosity, the lower the yield, although it should be noted that the viscosity does not correspond to that of the actual catalytic system but of the neat IL at ambient temperature and consequently this correlation should be treated with caution.

4. Conclusions

In conclusion, the imidazolium tetrachloropalladate salts **1b**, **2b** and **3b** are reasonable pre-catalysts for Suzuki cross-coupling reactions in ILs. The cation influences the efficiency of the reaction with the largest polycyclic system studied providing highest activities. This effect could be due to graphitic-like π interactions with the surface of palladium nanoparticles.

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