

# Development of Nitrile-Functionalized Ionic Liquids for C–C Coupling Reactions: Implication of Carbene and Nanoparticle Catalysts

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A series of nitrile-functionalized imidazolium salts (many of which are liquid at room temperature) have been prepared. The reactivity of these salts with PdCl<sub>2</sub> has been studied, resulting in salts containing a tetrachloropalladate dianion or compounds in which the nitrile substituent coordinates to the palladium center. Further derivation of the latter compounds affords carbenes. All the new compounds have been characterized by spectroscopic methods and nine of them by single-crystal X-ray diffraction. The catalytic activity of the different palladium salts in Suzuki, Stille, and Heck reactions has been evaluated in some of the nitrile-functionalized ionic liquids (ILs) and compared with that of nonfunctionalized ILs, providing insights into the nature of the actual catalyst. In some instances, palladium nanoparticles have been identified, but the nature of the catalyst strongly depends on the IL employed.

## Introduction

The application of ILs in synthesis and catalysis,<sup>1</sup> as well as numerous other areas,<sup>2</sup> is currently attracting considerable attention. One of the most attractive features of ILs is that both the cationic and anionic components can be varied, allowing ILs to be modified for specific applications. The term task-specific IL (TSIL) was introduced,<sup>3</sup> in order to describe low-melting salts with functional groups that provide particular, and ideally predictable, properties. A range of different functional groups that impart such properties have already been incorporated into IL cations, including vinyl and allyl,<sup>4,5</sup> amine,<sup>6</sup> amide,<sup>7</sup> ether and alcohol,<sup>8</sup> acid,<sup>9</sup> urea and thiourea,<sup>3</sup> fluororous chains,<sup>10</sup>

glycidyl chains,<sup>11</sup> alkyne,<sup>12</sup> phosphoryl,<sup>13</sup> nitrile,<sup>14</sup> thiols,<sup>15</sup> and ferrocenyl groups.<sup>16</sup> Numerous ILs with functional anions are also known, and examples of such anions include chiral anions,<sup>17</sup> carboranes,<sup>18</sup> metal carbonyls,<sup>19,20</sup> alkylselenites,<sup>21</sup> and functionalized borate anions.<sup>22</sup>

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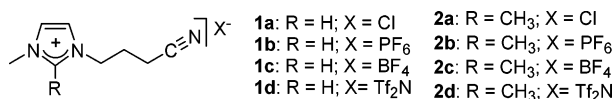
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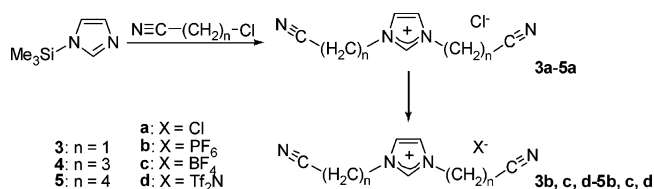
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**Figure 1.** Mono(nitrile)-functionalized imidazolium ILs.

**Scheme 1. Synthesis of Imidazolium Salts 3–5**



While the non-nucleophilic nature of many ILs seems to be advantageous in catalysis, providing a protective environment which can extend the catalyst lifetime,<sup>23</sup> it is becoming increasingly apparent that the design and synthesis of ILs that provide specific properties is becoming very attractive, where they are employed as immobilization media in multiphase catalysis, as the functional group can increase catalyst stability and/or improve catalyst retention. For example, we have previously described the application of some of the imidazolium salts shown in Figure 1 and salts based on the pyridinium cation which are functionalized with a nitrile moiety in various palladium-catalyzed cross-coupling reactions,<sup>24</sup> and numerous advantages were noted. As an extension of this work, herein we report the synthesis, structures, and performance of a series of mono(nitrile)- and bis(nitrile)-functionalized imidazolium-based ILs in Suzuki, Stille, and Heck reactions and evaluate the nature of the probable active catalyst.

**Results and Discussion**

The mono(nitrile)-functionalized ILs used in this study were reported previously,<sup>14</sup> and some of the bis(nitrile)-functionalized ILs (Scheme 1) were reported in preliminary form.<sup>24b</sup> In brief, the chloride salts **3a–5a** were prepared from the direct reaction of (trimethylsilyl)imidazole with 1-chloroalkylnitriles as shown in Scheme 1. The salts [(CCN)<sub>2</sub>im]Cl (**3a**; [(CCN)<sub>2</sub>im] = 1,3-bis(cyanomethyl)imidazolium) and [(C<sub>3</sub>CN)<sub>2</sub>im]Cl (**4a**; [(C<sub>3</sub>CN)<sub>2</sub>im] = 1,3-bis(cyanobutyl)imidazolium) are solids, whereas [(C<sub>4</sub>CN)<sub>2</sub>im]Cl (**5a**; [(C<sub>3</sub>CN)<sub>2</sub>im] = 1,3-bis(cyanopentyl)imidazolium) is a light brown viscous liquid.

Anion metathesis of the chlorides **3a–5a** with HPF<sub>6</sub>, NaBF<sub>4</sub>, or LiTf<sub>2</sub>N (Tf<sub>2</sub>N = bis(trifluoromethyl)sulfonylamide) affords the corresponding PF<sub>6</sub> (**3b–5b**), BF<sub>4</sub> (**3c–5c**), and Tf<sub>2</sub>N (**3d–5d**) derivatives, in high yield. Salts **3–5** were characterized using electrospray ionization mass spectrometry (ESI-MS), IR and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and elemental analysis. ESI-MS was used to establish the presence of the imidazolium cations and anions, and in all cases a peak of high relative intensity indicative of the parent cation and anion were observed. In the positive mode, anion–cation aggregates comprising [(Cation)<sub>3</sub>(Anion)<sub>2</sub>]<sup>+</sup> and [(Cation)<sub>4</sub>(Anion)<sub>3</sub>]<sup>+</sup> are observed in samples of ca. 10<sup>−3</sup>–10<sup>−4</sup> M, whereas for simple ionic liquids, i.e., 1-butyl-3-methylimidazolium salts, the main peak corresponds to [(Cation)<sub>2</sub>Anion]<sup>+</sup> (under identical conditions).

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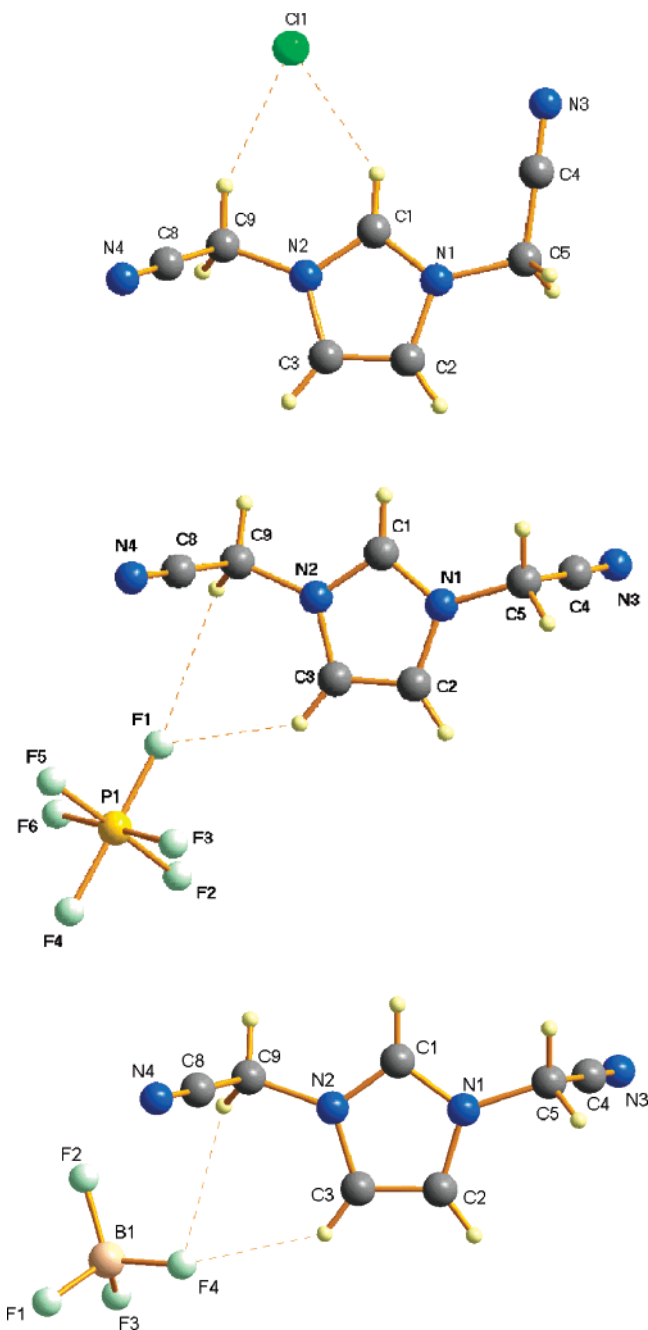
However, at lower concentration (10<sup>−6</sup> M) only the isolated parent ions [Cation]<sup>+</sup> are observed. The reason for the increased tendency of anion–cation aggregation in the nitrile-functionalized ILs could be due to the electron-withdrawing effect of the CN group, which makes the aliphatic hydrogen atoms more acidic so that hydrogen bonding between the cation and anion is enhanced, and/or increased head-to-tail interaction of the CN group with the imidazolium ring. Moreover, σ–π interactions between the CN group (σ-donor) and imidazolium rings have been observed in a previous investigation.<sup>14</sup> The C≡N vibration in the IR spectra of **3–5** increases in wavenumber as the length of the alkyl chain decreases, i.e., from 2245 cm<sup>−1</sup> in **5a** to 2263 cm<sup>−1</sup> in **3a**, and is independent of the nature of the anion. The <sup>1</sup>H NMR spectra of **3a–5a** exhibit the characteristic resonance of the imidazolium protons, and minor changes are observed in the chemical shifts in the alkyl protons. In D<sub>2</sub>O the proton at the 2-position in the compound **3a** is rapidly exchanged by deuterium at room temperature. Even the protons in the side arms (the two CH<sub>2</sub>CN groups) undergo fast H–D exchange at room temperature. In an experiment containing a sample of compound **3a** (50 mg in D<sub>2</sub>O, 0.5 mL), the signal of 2-H disappeared in less than 15 min at room temperature. The signals of the protons in the side arms disappeared in less than 24 h. The fast H–D exchange is presumably due to the electron-withdrawing effect of the nitrile functionality and of the positively charged imidazolium group. The rate of H–D exchange in D<sub>2</sub>O at room temperature (for the 2-H) is slower for **4a** and **5a**, in which the alkyl chains are longer, and no H–D exchange can be observed for the protons in the side arm.

Most of the bis(nitrile)-functionalized imidazolium salts have melting points below 100 °C, and six of them (**4c,d** and **5a–d**) are liquids at room temperature. In general, as the length of the alkyl chain between the imidazolium cation and nitrile functionality increases, the melting point decreases. More importantly, however, is that the viscosities of the bis(nitrile)-functionalized ILs that are liquid at ambient temperatures are higher than those of the related “single-armed” salts.

Single crystals of **3a–c** and **4a,b** were obtained from acetonitrile solutions by slow diffusion with diethyl ether, and their molecular structures have been determined by X-ray diffraction. The structures of **3a–c** and **4a,b** are depicted in Figures 2 and 3, respectively, and key parameters for all of the structures are collected in Table 1. All five salts are similar and differ mainly with respect to the orientation of the nitrile chain relative to the imidazolium ring, as can be appreciated from Figure 4. In all five structures, the imidazolium ring is almost perfectly planar; bond angles in the rings range from 106.3(5) to 109.9(5)° and distances from 1.313(7) to 1.406(6) Å. The –CH<sub>2</sub>C≡N moiety is essentially linear, with the C–N distance (1.129(5)–1.171(7) Å) being found in the expected range.<sup>14,24b,25</sup>

Extensive hydrogen bonding is present in all the structures, and it is interesting to note that, in agreement with the observed melting points, significantly shorter hydrogen bonds are found in the hexafluorophosphate salts **3b** and **4b** than in the corresponding chloride salts. In **3a** there are four hydrogen contacts to the chloride below 3 Å, ranging from 2.535 to 2.907 Å, while there are 13 hydrogen contacts to the F atoms below 3 Å in **3b**, ranging from 2.280 to 2.903 Å. Caution must be applied in correlating the melting point with the number and distance of H···X bonds, as the tetrafluoroborate salt **3c** has 11 contacts ranging from 2.322 to 2.806 Å yet has a lower melting

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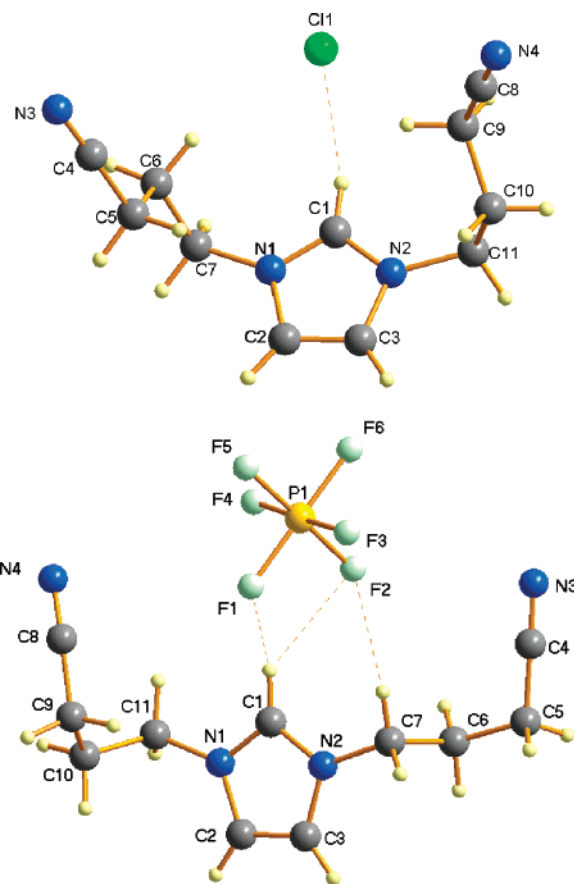


**Figure 2.** Ball-and-stick representations of (top) **3a**, (middle) **3b**, and (bottom) **3c**. Spheres are of arbitrary radii.

point than **3a** (representations of the crystal packing and hydrogen bonding of **3a–c** are provided in the Supporting Information). The presence of the nitrile group in the imidazolium salts, especially in those where the short  $-\text{CH}_2\text{CN}$  moiety is attached to the imidazolium core (**3a–c**), increase the cation–anion interactions via hydrogen bondings, due to the increased acidity of the hydrogen atoms in the  $-\text{CH}_2\text{CN}$  unit. This feature further explains why the H–D exchange of **3a** in  $\text{D}_2\text{O}$  takes place so readily. A similar phenomenon has also been observed in related systems.<sup>26</sup>

**Synthesis of  $[\text{PdCl}_4]^{2-}$  Salts.** Acetonitrile solutions of **1a**, **2a**, and **4a** were treated with  $\text{PdCl}_2$ , affording the corresponding  $[\text{PdCl}_4]^{2-}$  salts  $[(\text{C}_3\text{CNmim})_2][\text{PdCl}_4]$  (**6a**),  $[(\text{C}_3\text{CNDmim})_2][\text{PdCl}_4]$  (**7a**), and  $[(\text{C}_3\text{CNdim})_2][\text{PdCl}_4]$  (**8a**), as outlined in

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**Figure 3.** Ball-and-stick representations of (top) **4a** and (bottom) **4b**. Spheres are of arbitrary radii.

**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for **3a–c** and **4a,b**

	<b>3a</b>	<b>3b</b>	<b>3c</b>	<b>4a</b>	<b>4b</b>
C1–N1	1.337(8)	1.327(4)	1.333(2)	1.313(7)	1.335(3)
C1–N2	1.337(8)	1.340(4)	1.330(2)	1.337(7)	1.331(3)
C2–N1	1.401(8)	1.384(4)	1.380(2)	1.406(6)	1.374(3)
C3–N2	1.398(8)	1.378(4)	1.388(2)	1.382(7)	1.379(3)
C2–C3	1.349(9)	1.351(4)	1.346(3)	1.356(8)	1.349(3)
N3–C4	1.137(10)	1.147(4)	1.143(2)	1.171(7)	1.145(3)
N4–C8	1.134(9)	1.145(4)	1.144(2)	1.155(7)	1.129(5)
N3–C4–C5	179.8(8)	178.0(3)	178.3(2)	178.4(7)	178.9(3)
N4–C8–C9	178.7(7)	178.7(3)	178.3(2)	179.4(6)	177.4(4)
N1–C1–N2	109.9(5)	107.1(3)	107.9(2)	109.6(5)	108.5(2)

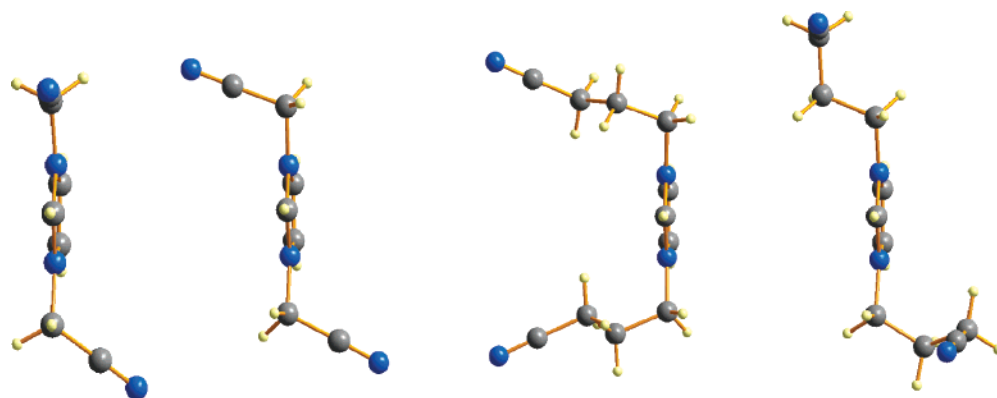
Scheme 2. Dichloromethane can also be used as a solvent, but the reaction is very slow at room temperature and requires several days to reach completion. Despite the potential of the nitrile pendant group attached to the IL cation to coordinate to palladium, the palladium(II) center reacts exclusively with the chloride counteranion. As has been shown elsewhere,<sup>27</sup> chloride is poorly solvated in ILs and has enhanced nucleophilicity.

In contrast to the chloride salts, ILs **1b–d** and **2b–d** react with  $\text{PdCl}_2$  in a 2:1 molar ratio in dichloromethane at room temperature to form complexes in which the nitrile group is coordinated to the palladium center: viz.,  $[(\text{C}_3\text{CNmim})_2\text{PdCl}_2][\text{PF}_6]_2$  (**6b**),  $[(\text{C}_3\text{CNDmim})_2\text{PdCl}_2][\text{BF}_4]_2$  (**6c**), and  $[(\text{C}_3\text{CNmim})_2\text{PdCl}_2][\text{Tf}_2\text{N}]_2$  (**6d**) and  $[(\text{C}_3\text{CNDmim})_2\text{PdCl}_2][\text{PF}_6]_2$  (**7b**),  $[(\text{C}_3\text{CNDmim})_2\text{PdCl}_2][\text{BF}_4]_2$  (**7c**), and  $[(\text{C}_3\text{CNDmim})_2\text{PdCl}_2][\text{Tf}_2\text{N}]_2$  (**7d**) (see Scheme 3).

The compounds  $[(\text{C}_3\text{CNmim})_2][\text{PdCl}_4]$  (**6a**) and  $[(\text{C}_3\text{CNDmim})_2][\text{PdCl}_4]$  (**7a**) react with further  $\text{PdCl}_2$  in a 1:1 molar ratio in

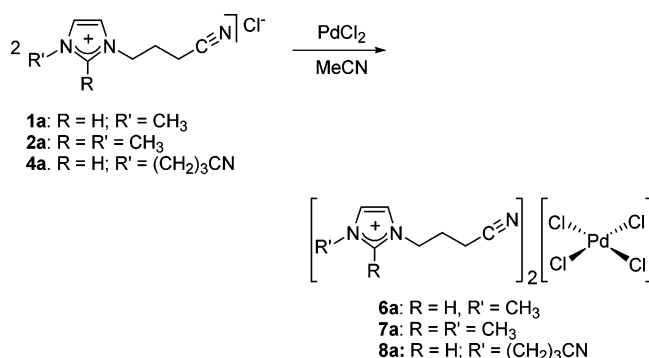
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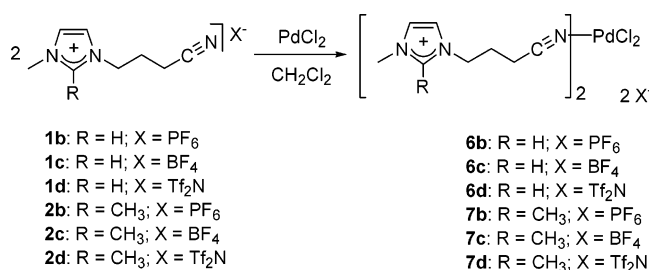


**Figure 4.** Ball-and-stick representations of **3a,b** and **4a,b** (from left to right, respectively), showing the different orientations of the side chains in the crystals.

### Scheme 2. Synthesis of Palladium Complexes **6a–8a**



### Scheme 3. Synthesis of Palladium Complexes **6b–d/7b–d**



dichloromethane to form  $[(\text{C}_3\text{CNmim})_2\text{PdCl}_2][\text{PdCl}_4]$  (**9**) and  $[(\text{C}_3\text{CNdmim})_2\text{PdCl}_2][\text{PdCl}_4]$  (**10**), which can be viewed as hybrids of the two types of complexes described above. Spectroscopic characterization of the palladium salts by <sup>1</sup>H and <sup>13</sup>C NMR provides only limited information, as the chemical shift of the imidazolium ring is not very sensitive to coordination. The IR spectra are more informative, with the stretching vibration of the C≡N group remaining essentially unchanged in **6a–8a** (2241, 2244, 2249 cm<sup>-1</sup>), relative to the imidazolium precursors (see above). In the complexes where the nitrile moiety coordinates to the palladium center, namely **6b–d**, **7b–d**, **9**, and **10**, the  $\nu_{\text{C}\equiv\text{N}}$  stretching band is observed at higher wavenumbers (2300–2325 cm<sup>-1</sup>).

Compounds **6a–8a** are soluble in acetonitrile and may be crystallized by addition of diethyl ether. In contrast, complexes **6b–d** and **7b–d** are unstable and convert to **1b–d** and **2b–d** with the concomitant formation of Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub>. Salts **9** and **10** also revert back to **6a** and **7a** and Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> in acetonitrile. The structures of **6a–8a** are shown in Figure 5, and selected bond lengths and angles are given in Table 2. The structures of the cations do not change significantly upon reaction of the imidazolium chloride with PdCl<sub>2</sub> and are comparable to those described above. In all three structures the

$[\text{PdCl}_4]^{2-}$  anion has a regular square-planar geometry with Cl–Pd–Cl angles ranging between 88.67(2) and 91.33(2)°. The coordination plane of the  $[\text{PdCl}_4]^{2-}$  anion in **6a–8a** is tilted by 123.0, 74.4, and 123.6°, respectively, relative to the mean plane of the imidazolium rings. Although there are numerous interactions between the hydrogens and the chlorides, these are, as expected, generally much longer than those observed in the salts containing perfluorinated anions. The shortest hydrogen bond is found in **8a**, stemming from H2 to Cl1 (2.564 Å). In **6a** and **7a** there are additional close contacts from hydrogen atoms to the metal center: H5B⋯Pd1 = 2.671 Å in **6a** and H12C⋯Pd1 = 2.763 Å in **7a**.

More generally, palladium(II) compounds are widely used as catalyst precursors for a wide range of different reactions, notably C–C coupling reactions,<sup>28</sup> and with this in mind the catalytic activity of some of these palladium salts has been investigated in Suzuki, Heck, and Stille coupling reactions (see below). However, since carbenes have been implicated in C–C coupling reactions,<sup>29,30</sup> the carbene complex  $[(\text{C}_3\text{CN})_2\text{im}]_2\text{PdCl}_2$  (**11**) was prepared and tested for catalytic activity. The preparation of **11** is straightforward, involving reaction of **8a** with Ag<sub>2</sub>O. The <sup>13</sup>C NMR spectrum of **11** displays a characteristic peak for 2-C (carbene atom) at 169.5 ppm. Single crystals suitable for X-ray analysis can be obtained by slow evaporation of diethyl ether into a solution of acetonitrile (Figure 6). For **11** in the solid state, the coordination sphere around the Pd center is square planar, with a trans arrangement of the carbene ligands. The Pd1–C1 and Pd1–Cl1 bond distances are 2.033(3) and 2.3157(7) Å, respectively, which are comparable to similar trans-Pd imidazolium–carbene complexes with chloride coligands.<sup>31</sup> The imidazolium rings are oriented almost perpendicular to the Pd coordination plane, in order to relieve the steric hindrance encumbered by the pendant cyanobutyl arms.

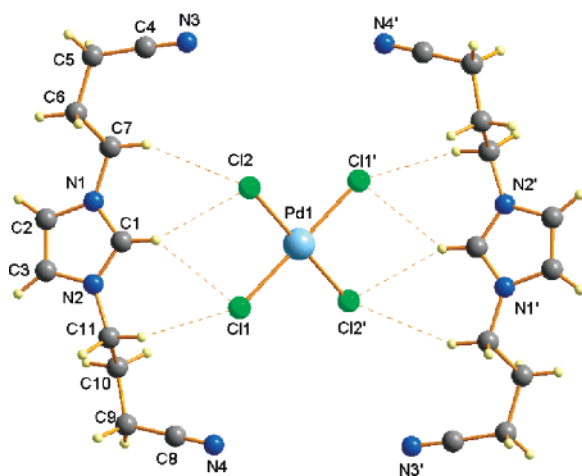
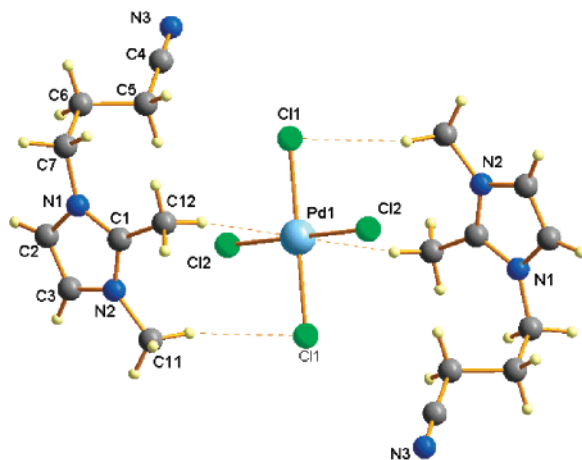
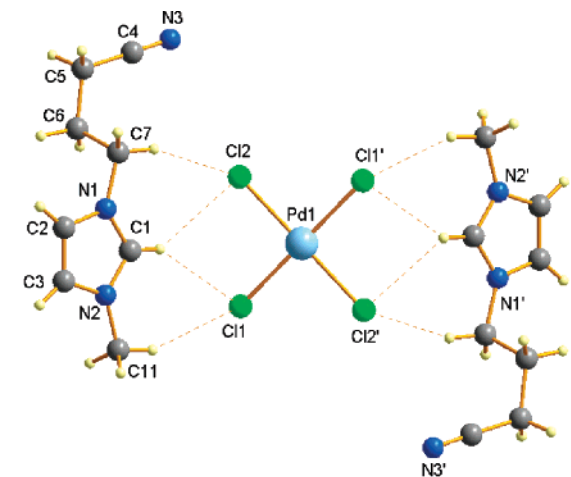
**Carbon–Carbon Coupling Reactions.** Suzuki cross-coupling reactions in  $[\text{C}_4\text{mim}][\text{BF}_4]$  using Pd(PPh<sub>3</sub>)<sub>4</sub> as the catalyst have been reported previously, and a number of benefits have

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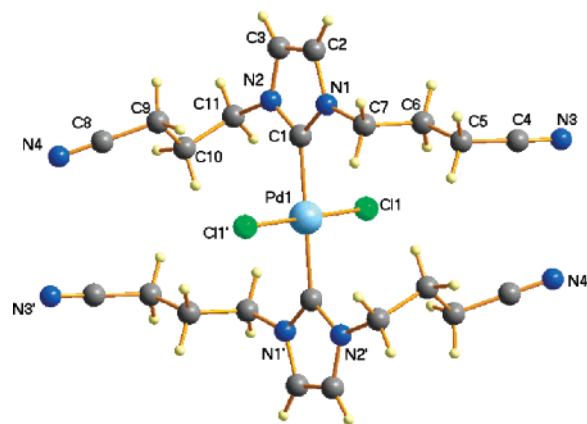


**Figure 5.** Ball-and-stick representations of (top) **6a**, (middle) **7a**, and (bottom) **8a**. Spheres are of arbitrary radii.

been noted compared to reactions in organic solvents, including increased rates and selectivities, as well as operating under milder conditions and facilitating catalyst recycling.<sup>32</sup> Palladium(II) salts such as Pd(OAc)<sub>2</sub> and PdCl<sub>2</sub> have also been used as precatalysts in Suzuki reactions without requiring added coligands.<sup>33</sup> 1-Alkyl-3-methylimidazolium chloropalladate salts, [C<sub>n</sub>mim]<sub>2</sub>[PdCl<sub>4</sub>],<sup>34</sup> dissolved in ILs have also been used to

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(33) Deng, Y.; Gong, L.; Mi, A.; Liu, H.; Jiang, Y. *Synthesis* **2003**, 3, 337.



**Figure 6.** Ball-and-stick representation of **11**. Spheres are of arbitrary radii.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Compounds **6a–8a** and **11**

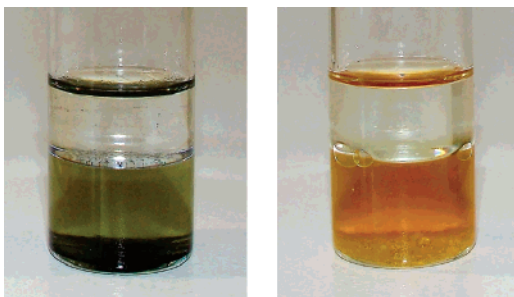
	<b>6a</b>	<b>7a</b>	<b>8a</b>	<b>11</b>
Pd1–Cl1	2.3147(6)	2.3229(5)	2.3113(6)	2.3157(7)
Pd1–Cl2	2.3113(6)	2.3177(5)	2.3205(7)	
C1–N1	1.335(3)	1.351(3)	1.333(3)	1.347(3)
C1–N2	1.333(3)	1.336(3)	1.339(3)	1.354(3)
C2–N1	1.384(3)	1.387(3)	1.384(3)	1.390(3)
C3–N2	1.385(3)	1.383(3)	1.380(3)	1.385(4)
C2–C3	1.349(4)	1.349(3)	1.356(4)	1.341(4)
N3–C4	1.141(3)	1.148(3)	1.143(4)	1.136(4)
N4–C8			1.143(4)	1.137(4)
N3–C4–C5	178.9(3)	177.8(3)	177.9(3)	178.3(3)
N4–C8–C9			179.4(3)	178.6(3)
N1–C1–N2	108.5(2)	107.2(2)	108.7(2)	104.5(2)

catalyze 1,3-butadiene hydrodimerization.<sup>35</sup> Thus, we thought it would be interesting to study the influence of the palladium species and the IL on model C–C coupling reactions.

The Suzuki reaction between phenyl iodide and phenylboronic acid was conducted in the presence of 1.2 mol % of PdCl<sub>2</sub>, [(C<sub>3</sub>CNdmim)<sub>2</sub>][PdCl<sub>4</sub>] (**6a**), or [(C<sub>3</sub>CNdmim)<sub>2</sub>PdCl<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (**7b**) in [C<sub>4</sub>mim][BF<sub>4</sub>], [C<sub>3</sub>CNmim][BF<sub>4</sub>] (**1c**), or [(C<sub>3</sub>CN)<sub>2</sub>im][BF<sub>4</sub>] (**4c**), with sodium carbonate as base (see the Experimental Section for full details). Under the reaction conditions used, essentially quantitative conversion to biphenyl was observed in all cases. Both the yields of the coupling and the retention of the catalyst are not sensitive to the source of the palladium employed and depend mainly on the nature of the solvent in use. The most notable difference observed between [C<sub>4</sub>mim][BF<sub>4</sub>] and the functionalized ILs is the extent of palladium leaching observed, which is always considerably higher for [C<sub>4</sub>mim][BF<sub>4</sub>] than for the ILs bearing nitrile functionalities (~100 ppm for [C<sub>4</sub>mim]BF<sub>4</sub>, ~5 ppm for **1c**, and <1 ppm for **4c**). The introduction of a second nitrile group on the cation further increases the retention capability of the solvent. The difference between using nitrile-functionalized and nonfunctionalized ILs can also be appreciated from Figure 7, which shows that in [C<sub>4</sub>mim][BF<sub>4</sub>] the formation of palladium black is observed, whereas in [C<sub>3</sub>CNmim][BF<sub>4</sub>] (**1c**) no such decomposition is observed. The difference between reactions conducted in functionalized ILs with respect to the nonfunctionalized ILs is also apparent in the recycling tests, where the activity of the catalytic system does not change after six runs in [C<sub>3</sub>CNmim][BF<sub>4</sub>] (**1c**), whereas the [C<sub>4</sub>mim][BF<sub>4</sub>]-palladium systems are

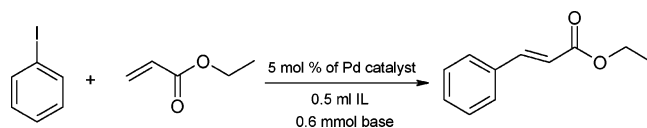
(34) Hardacre, C.; Holbrey, J. D.; McCormac, P. B.; McMath, S. E. J.; Nieuwenhuyzen, M.; Seddon, K. R. *J. Mater. Chem.* **2001**, *11*, 346.

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**Figure 7.** Comparison of product phase and catalysis immobilization phase following catalysis (after the first cycle): (left) PdCl<sub>2</sub> in [C<sub>4</sub>mim][BF<sub>4</sub>]; (right) PdCl<sub>2</sub> in [C<sub>3</sub>CNmim][BF<sub>4</sub>].

**Table 3.** Heck Coupling of Iodobenzene with Ethyl Acrylate in [C<sub>3</sub>CNmim][Tf<sub>2</sub>N] (**1d**) at 80 °C



	cat.	base	time, h	additive	yield, % <sup>a</sup>
1	PdCl <sub>2</sub>	[cholinium][OAc]	12	HCOONH <sub>4</sub>	>99
2	PdCl <sub>2</sub>	[cholinium][OAc]	1	HCOONH <sub>4</sub>	85
3	PdCl <sub>2</sub>	[cholinium][OAc]	12		65
4	PdCl <sub>2</sub>	[cholinium][OAc]	6		58
5	PdCl <sub>2</sub>	[cholinium][OAc]	3		49
6	PdCl <sub>2</sub>	[cholinium][OAc]	2		51
7	PdCl <sub>2</sub>	[cholinium][OAc]	1		42
8	PdCl <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	12		16
9	<b>6a</b>	[cholinium][OAc]	12	HCOONH <sub>4</sub>	99
10	<b>6a</b>	[cholinium][OAc]	12		70
11	<b>6a</b>	Na <sub>2</sub> CO <sub>3</sub>	12		32

<sup>a</sup> Determined by GC analysis using 3-methoxyacetophenone as standard.

inactive after three cycles. Thus, irrespective of the true identity of the catalyst, the nitrile-functionalized ILs increase the stability of the catalyst and improve catalyst retention, both phenomena contributing to increased catalyst lifetimes.

Heck reactions have been extensively investigated in ILs with numerous advantages demonstrated,<sup>36</sup> and therefore, the Heck reaction between iodobenzene and ethyl acrylate in the presence of PdCl<sub>2</sub> was studied in the ILs described herein. Preliminary data showed a low reactivity of the catalytic system using both functionalized and nonfunctionalized ILs, with a maximum of 51% of conversion in 24 h at 100 °C using sodium acetate as base. The low reactivity of the system could be ascribed to several factors, including the poor solubility of the base in the ionic medium, a high stabilization of palladium as [PdCl<sub>4</sub>]<sup>2-</sup> or by coordination of the nitrile group, or rapid inactivation of the catalytic system. To test these hypotheses, the coupling was performed in the presence of HCOONH<sub>4</sub>/Et<sub>3</sub>N as a reducing agent, using different palladium sources (see Table 3). Among the ILs available, [C<sub>3</sub>CNmim][Tf<sub>2</sub>N] (**1d**) was selected as the first candidate, together with the corresponding nonfunctional-

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**Table 4.** Cross-Coupling of Iodobenzene with Ethyl Acrylate at 80 °C for 1 h in Several [Tf<sub>2</sub>N]-Based ILs, Using [cholinium][OAc] as the Base

	solvent	cat.	yield, % <sup>a</sup>
1	[C <sub>4</sub> mim][Tf <sub>2</sub> N]	PdCl <sub>2</sub>	45
2	[Camim][Tf <sub>2</sub> N]	<b>6a</b>	35
3	[C <sub>3</sub> CNmim][Tf <sub>2</sub> N] ( <b>1d</b> )	PdCl <sub>2</sub>	55
4	[C <sub>3</sub> CNmim][Tf <sub>2</sub> N] ( <b>1d</b> )	<b>6a</b>	33
5	[(C <sub>3</sub> CN) <sub>2</sub> im][Tf <sub>2</sub> N] ( <b>4d</b> )	PdCl <sub>2</sub>	60
6	[(C <sub>3</sub> CN) <sub>2</sub> im][Tf <sub>2</sub> N] ( <b>4d</b> )	<b>6a</b>	48

<sup>a</sup> Determined by GC analysis using 3-methoxyacetophenone as standard; selectivity to *trans*-ethyl cinnamate was quantitative in all reactions, as determined by <sup>1</sup>H NMR.

ized IL [C<sub>4</sub>mim][Tf<sub>2</sub>N]. As expected, in the presence of HCOONH<sub>4</sub>, almost quantitative conversion of iodobenzene into cinnamate was obtained, irrespective of the catalyst used (entries 1 and 9 in Table 3). Moreover, the [cholinium][OAc] base is superior to Na<sub>2</sub>CO<sub>3</sub>, presumably because it ensures a homogeneous reaction mixture.

The carbene complex [(C<sub>3</sub>CN)<sub>2</sub>im]<sub>2</sub>PdCl<sub>2</sub> (**11**) was also tested as a catalyst/catalyst precursor under comparable conditions, but activities were very low: ca. 2–8% conversion under comparable conditions (see the Supporting Information). In order to investigate the effect of the solvent on the reaction investigated, the coupling was performed in several ILs for comparison purposes, and the corresponding data are presented in Table 4.

It can be seen from the table that both PdCl<sub>2</sub> and [(C<sub>3</sub>CNdmim)<sub>2</sub>][PdCl<sub>4</sub>] (**6a**) are active precatalysts in the Heck reaction, affording *trans*-ethyl cinnamate as the only product (no biphenyl could be detected). In all cases PdCl<sub>2</sub> is more effective than **6a**, presumably because the [PdCl<sub>4</sub>]<sup>2-</sup> less readily converts to the active catalyst, since it is coordinatively saturated by chloride ligands. Dissolving PdCl<sub>2</sub> in the nitrile-functionalized ILs presumably affords nitrile-coordinated complexes (see above). In addition, the efficiency of the reaction increases according to the series [C<sub>4</sub>mim][Tf<sub>2</sub>N] < [C<sub>3</sub>CNmim][Tf<sub>2</sub>N] (**1d**) < [(C<sub>3</sub>CN)<sub>2</sub>im][Tf<sub>2</sub>N] (**4d**), indicating the importance of the stabilizing influence of the nitrile groups that was also noted for the Suzuki reactions.

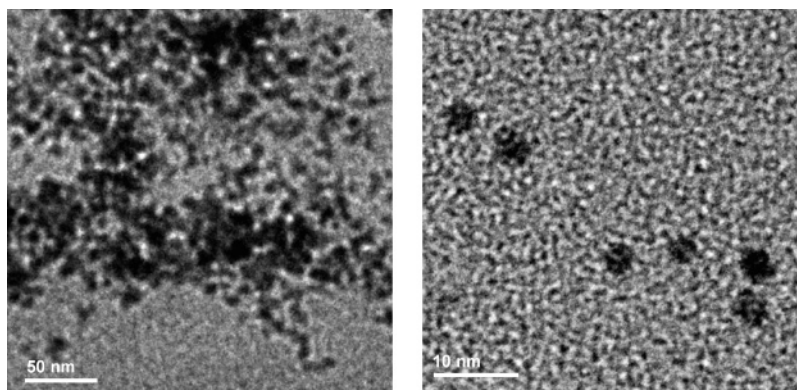
Reuse of the IL systems was not very encouraging, with a progressive loss of activity (from near-quantitative to ca. 20% conversion on the fourth run; see the Supporting Information). The decrease in reactivity of the catalyst could be ascribed to the consumption of the base and addition of 1 equiv of cholinium acetate after the fourth cycle restored the reactivity of the system.

The Stille reaction<sup>37</sup> has also been reported in ILs in the absence of cocatalysts.<sup>24,38</sup> The Stille coupling reaction of tributylvinylstannane with iodobenzene was investigated, and in keeping with previous observations, PdCl<sub>2</sub> is a more effective catalyst precursor than [(C<sub>3</sub>CNdmim)<sub>2</sub>][PdCl<sub>4</sub>] (**6a**) (see the Supporting Information). The highest conversion of 96% was obtained with PdCl<sub>2</sub> in [(C<sub>3</sub>CN)<sub>2</sub>im][BF<sub>4</sub>] (**4c**); with the more coordinating Tf<sub>2</sub>N anion somewhat lower activities were observed, presumably due to stronger interactions of the anion with the metal center, which impedes catalysis slightly. In the nitrile-functionalized ILs palladium could not be detected by ICP in the organic phase, indicating <1 ppm is present.

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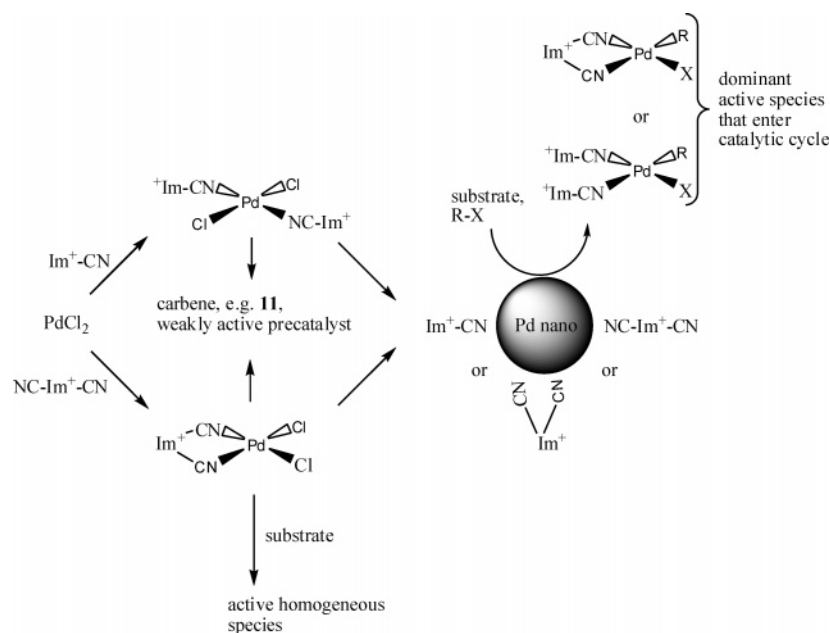
(38) (a) Liu, S.; Fukuyama, T.; Sato, M.; Ryu, I. *Synlett* **2004**, 1814. (b) Chiappe, C.; Imperato, G.; Napolitano, E.; Pieraccini, D. *Green Chem.* **2004**, 6, 33. (c) Handy, S. T.; Zhang, X. *Org. Lett.* **2001**, 3, 233.





**Figure 8.** Comparison of TEM images of the Pd nanoparticles isolated following catalysis from (left)  $[\text{C}_4\text{mim}][\text{BF}_4]$  and (right)  $[\text{C}_3\text{CNmim}][\text{BF}_4]$  (**1c**).

#### Scheme 4



Transmission electron microscopy (TEM) was used to determine the presence (or absence) of nanoparticles immobilized in the ILs after catalysis. Evidence has accumulated to show that many C–C coupling reactions involve palladium nanoparticles, especially when simple metal salts, for example, palladium(II) halides, are used as the catalyst precursors.<sup>39</sup> The use of ionic liquids has helped to establish the role of nanoparticles in C–C coupling reactions,<sup>40</sup> although challenges remain. Palladium nanoparticles were isolated from  $[\text{C}_4\text{mim}][\text{BF}_4]$  and  $[\text{C}_3\text{CNmim}][\text{BF}_4]$  (**1c**) following the Stille reaction (Figure 8), but it was not possible to isolate nanoparticles from the bis-functionalized nitrile IL  $[(\text{C}_3\text{CN})_2\text{im}][\text{BF}_4]$  (**4c**).

The nanoparticles isolated from  $[\text{C}_4\text{mim}][\text{BF}_4]$  and  $[\text{C}_3\text{CNmim}][\text{BF}_4]$  have a similar diameter of ca. 5 nm, but they show different morphologies. The nanoparticles obtained from **1c** are well-separated, whereas those from  $[\text{C}_4\text{mim}][\text{BF}_4]$  are

aggregated, forming nanoclusters up to ca. 30 nm. It is plausible that the nitrile group interacts weakly with the palladium nanoparticle surface, exerting a stabilizing effect and preventing aggregation. However, palladium nanoparticles are reservoirs for mononuclear Pd(II) species, believed to be the true active catalyst,<sup>41</sup> and it is conceivable that the nitrile-functionalized ILs also help to stabilize such intermediates via transient coordination of the nitrile group (see Conclusions). Palladium leaching into the organic extract was also found to be about 10 times lower in the nitrile-functionalized ILs, which combined lead to excellent recycling of the system. The yield of the Stille product can be maintained around 90% in the nitrile-functionalized ILs (see the Supporting Information).

#### Conclusions

The series of nitrile-functionalized ILs and palladium complexes described herein provide insights into the nature of the active catalyst in various C–C coupling reactions (Scheme 4). Essentially the nitrile-functionalized ILs facilitate solubility of the  $\text{PdCl}_2$  precatalyst via weak coordination of the nitrile groups. If the anion is a strong nucleophile, such as chloride, then preferential coordination takes place, and the resulting complex

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(41) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 609.

is less catalytically active or, more likely, less able to transform to the active species. The palladium(II) complexes are readily reduced, giving palladium nanoparticles, although nanoparticles were not identified for the bis-functionalized ILs. This does not mean that they are not present, but it is conceivable that the bis-functionalized cation can chelate to palladium and stabilize a mononuclear catalyst.

Previously, nanoparticles prepared in  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$  have been shown to be active catalysts for alkene hydrogenation.<sup>42</sup> Other nanoparticles composed of rhodium,<sup>43</sup> platinum,<sup>44</sup> and gold<sup>45</sup> have also been reported, but in C–C coupling reactions nanoparticles are believed to act as reservoirs, releasing the catalytically active Pd(II) species following oxidative addition of the substrate. From the results reported herein it seems likely that the role of the nitrile group on the IL cation is twofold, first to help form a protective sheath around the nanoparticle, preventing aggregation and second, helping to stabilize the active Pd(II) catalyst as shown in Scheme 4. Also, it is such synergistic behavior that probably gives rise to the superior properties of the nitrile-functionalized ILs in the reactions described here. While homogeneous carbene species do not appear to be important here, it has been shown that carbenes are involved in nanoparticle stabilization in ILs,<sup>46</sup> and the possibility of carbenes fulfilling such a role in these systems is highly likely.

## Experimental Section

Compounds **1a–c** and **2a–c**,<sup>14</sup> **1d**,<sup>24b</sup> **4a/5a**,<sup>22</sup> and **4d/5d**<sup>24b</sup> were prepared according to literature methods. (Trimethylsilyl)imidazole, sodium tetrafluoroborate, hexafluorophosphoric acid, lithium bis((trifluoromethyl)sulfonyl)amide, and palladium dichloride were purchased from Aldrich. Synthesis of imidazolium salts and derived palladium complexes was performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. NMR spectra were obtained at 20 °C with a Bruker DMX 400 instrument using  $\text{SiMe}_4$  for  $^1\text{H}$  and  $^{13}\text{C}$  as external standards. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. ESI-MS spectra were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument. Samples were infused directly into the source at  $5 \mu\text{L min}^{-1}$  using a syringe pump. The spray voltage was set at 5 kV and the capillary temperature at 50 °C.<sup>47</sup> Elemental analysis was carried out at the EPFL. ICP-AES (inductively coupled plasma-atomic emission spectrometer) were analyzed on a Perkin-Elmer Optima 3000 ICP-AE spectrometer. Intensities of spectral lines at 340 and 458 nm were measured in all samples and standards. The Pd level in the samples was determined by comparing the intensity of the spectral line with a Pd standard curve. Each sample was measured three times, and the average Pd concentration level of these measurements is reported.

**Synthesis of Imidazolium Salts 2d and 3–5.** (a)  $[\text{C}_3\text{CNDmim}][\text{Tf}_2\text{N}]$  (**2d**). The salt **2a** (19.9 g, 0.1 mol) was dissolved in water (50 mL), and  $\text{Li}[\text{Tf}_2\text{N}]$  (28.7 g, 0.10 mol) was added at room temperature. The reaction mixture was stirred for 30 min. The resulting colorless hydrophobic liquid was washed with water ( $3 \times 30 \text{ mL}$ ) and dried under vacuum for 24 h. Yield: 34.6 g, 78%; Mp:  $-55.6 \text{ }^\circ\text{C}$ . ESI-MS (methanol,  $m/z$ ): positive ion, 164  $[\text{C}_3\text{CNDmim}]^+$ ; negative ion, 280  $[\text{Tf}_2\text{N}]^-$ .  $^1\text{H}$  NMR (acetone- $d_6$ ):

$\delta$  7.65 (s, 1H), 7.60 (s, 1H), 4.25 (t,  $J(\text{H,H}) = 7.0 \text{ Hz}$ , 2H), 3.93 (s, 3H), 2.80 (s, 3H), 2.65 (t,  $J(\text{H,H}) = 7.0 \text{ Hz}$ , 2H), 2.30 (m, 2H).  $^{13}\text{C}$  NMR (acetone- $d_6$ ):  $\delta$  123.3, 122.3, 120.0, 46.7, 34.7, 25.5, 13.5, 8.5. IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$ , 2251. Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{F}_6\text{N}_4\text{O}_4\text{S}_2$ : C, 29.73; H, 3.18; N, 12.61. Found: C, 29.92; H, 3.15; N, 12.57.

(b)  $[(\text{CCN})_2\text{im}][\text{Cl}]$  (**3a**). A mixture of (trimethylsilyl)imidazole (14.03 g, 0.10 mol) and  $\text{ClCH}_2\text{CN}$  (15.10 g, 0.20 mol) was stirred at room temperature for 24 h, during which time the reaction mixture turned into a solid. The white solid was washed with diethyl ether ( $3 \times 30 \text{ mL}$ ). The solid product was dried under vacuum for 24 h. Yield: 17.3 g, 95%. Mp:  $176 \text{ }^\circ\text{C}$ . ESI-MS ( $\text{H}_2\text{O}$ ,  $m/z$ ): positive ion, 147  $[(\text{CCN})_2\text{im}]^+$ .  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta$  9.35 (s, 1H), 7.81 (s, 2H), 5.54 (s, 4H).  $^{13}\text{C}$  NMR ( $\text{D}_2\text{O}$ ): 138.2, 123.5, 113.4, 37.5. IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$ , 2263. Anal. Calcd for  $\text{C}_7\text{H}_7\text{ClN}_4$ : C, 46.04; H, 3.86; N, 30.68. Found: C, 46.08; H, 3.82; N, 30.65.

(c)  $[(\text{CCN})_2\text{im}][\text{PF}_6]$  (**3b**). The salt **3a** (18.2 g, 0.1 mol) was dissolved in water (50 mL), and  $\text{HPF}_6$  (24.3 g, 60 wt % aqueous solution, 0.10 mol) was added at room temperature. The resulting white hydrophobic solid was washed with cold water ( $3 \times 10 \text{ mL}$ ) and dried under vacuum for 24 h. Yield: 19.8 g, 68%. Mp:  $208 \text{ }^\circ\text{C}$ . ESI-MS (methanol,  $m/z$ ): positive ion, 147  $[(\text{CCN})_2\text{im}]^+$ ; negative ion, 145  $[\text{PF}_6]^-$ .  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  9.62 (s, 1H), 8.15 (s, 2H), 5.80 (s, 4H).  $^{13}\text{C}$  NMR (acetone- $d_6$ ):  $\delta$  131.1, 123.9, 113.2, 37.5. IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$ , 2262. Anal. Calcd for  $\text{C}_7\text{H}_7\text{F}_6\text{N}_4\text{P}$ : C, 28.78; H, 2.42; N, 19.18. Found: C, 28.75; H, 2.55; N, 19.16.

(d)  $[(\text{CCN})_2\text{im}][\text{BF}_4]$  (**3c**). The salt **3a** (18.2 g, 0.1 mol) was mixed with  $\text{NaBF}_4$  (10.98 g, 0.10 mol) in acetone and stirred at room temperature for 24 h. After filtration and removal of the solvent, the resulting pale yellow solid was washed with THF ( $2 \times 10 \text{ mL}$ ) and diethyl ether ( $3 \times 10 \text{ mL}$ ) to give the product. It was recrystallized from acetonitrile to give colorless crystals, which were collected by filtration. Yield: 14.9 g, 64%. Mp:  $110 \text{ }^\circ\text{C}$ ; ESI-MS (methanol,  $m/z$ ): positive ion, 147  $[(\text{CCN})_2\text{im}]^+$ ; negative ion, 87  $[\text{BF}_4]^-$ .  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  9.29 (s, 1H), 7.77 (s, 2H), 5.48 (s, 4H).  $^{13}\text{C}$  NMR (acetone- $d_6$ ):  $\delta$  131.1, 123.5, 113.3, 37.4. IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$  2258. Anal. Calcd for  $\text{C}_7\text{H}_7\text{BF}_4\text{N}_4$ : C, 35.94; H, 3.02; N, 23.95. Found: C, 35.99; H, 3.05; N, 23.86.

(e)  $[(\text{CCN})_2\text{im}][\text{Tf}_2\text{N}]$  (**3d**). The salt **3a** (18.2 g, 0.1 mol) was dissolved in water (50 mL), and  $\text{Li}[\text{Tf}_2\text{N}]$  (28.7 g, 0.10 mol) was added at room temperature. The reaction mixture was stirred for 2 h, and the resulting white hydrophobic solid was washed with water ( $3 \times 10 \text{ mL}$ ) and dried under vacuum for 24 h. Yield: 19.8 g, 68%. Mp:  $68 \text{ }^\circ\text{C}$ . ESI-MS (methanol,  $m/z$ ): positive ion, 147  $[(\text{CCN})_2\text{im}]^+$ ; negative ion, 280  $[\text{Tf}_2\text{N}]^-$ .  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  9.59 (s, 1H), 8.14 (s, 1H), 5.87 (s, 4H);  $^{13}\text{C}$  NMR (acetone- $d_6$ ):  $\delta$  131.1, 123.8, 113.2, 36.8. IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$  2262. Anal. Calcd for  $\text{C}_9\text{H}_7\text{F}_6\text{N}_5\text{O}_4\text{S}_2$ : C, 25.30; H, 1.65; N, 16.39. Found: C, 25.28; H, 1.70; N, 16.36.

(f)  $[(\text{C}_3\text{CN})_2\text{im}][\text{PF}_6]$  (**4b**). The salt **4a** (23.87 g, 0.1 mol) was dissolved in water (50 mL), and  $\text{HPF}_6$  (24.3 g, 60 wt % aqueous solution, 0.10 mol) was added at room temperature. The reaction mixture was stirred for 2 h, and the resulting white hydrophobic solid was filtered, washed with water ( $3 \times 10 \text{ mL}$ ), and dried under vacuum for 24 h. Yield: 20.2 g, 58%. Mp:  $79 \text{ }^\circ\text{C}$ . ESI-MS (methanol,  $m/z$ ): positive ion, 203  $[(\text{C}_3\text{CN})_2\text{im}]^+$ ; negative ion, 145  $[\text{PF}_6]^-$ .  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  9.18 (s, 1H), 7.86 (s, 2H), 4.53 (t,  $J(\text{H,H}) = 7.5 \text{ Hz}$ , 4H), 2.68 (t,  $J(\text{H,H}) = 7.5 \text{ Hz}$ , 4H), 2.38 (p,  $J(\text{H,H}) = 7.5 \text{ Hz}$ , 4H).  $^{13}\text{C}$  NMR (acetone- $d_6$ ):  $\delta$  136.6, 123.1, 111.5, 48.5, 25.7, 13.5. IR ( $\text{cm}^{-1}$ ):  $\nu_{\text{C}=\text{N}}$  2250. Anal. Calcd for  $\text{C}_{11}\text{H}_{15}\text{F}_6\text{N}_4\text{P}$ : C, 37.94; H, 4.34; N, 16.09. Found: C, 37.99; H, 4.38; N, 16.12.

(g)  $[(\text{C}_3\text{CN})_2\text{im}][\text{BF}_4]$  (**4c**). The salt **4a** (23.87 g, 0.1 mol) was mixed with  $\text{Na}[\text{BF}_4]$  (10.98 g, 0.10 mol) in acetone and stirred at room temperature for 24 h. After filtration and removal of the solvent, the resulting pale yellow liquid was washed with THF ( $3 \times 30 \text{ mL}$ ) and diethyl ether ( $3 \times 30 \text{ mL}$ ) and dried under vacuum

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for 24 h. Yield: 21.5 g, 74%. ESI-MS (methanol,  $m/z$ ): positive ion, 203 [(C<sub>3</sub>CN)<sub>2</sub>im]<sup>+</sup>; negative ion, 87 [BF<sub>4</sub>]<sup>-</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  9.12 (s, 1H), 7.83 (s, 2H), 4.49 (t,  $J$ (H,H) = 7.5 Hz, 4H), 2.65 (t,  $J$ (H,H) = 7.5 Hz, 4H), 2.35 (p,  $J$ (H,H) = 7.5 Hz, 4H). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>):  $\delta$  136.6, 123.01, 118.5, 48.4, 25.8, 13.5. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2248. Anal. Calcd for C<sub>11</sub>H<sub>15</sub>BF<sub>4</sub>N<sub>4</sub>: C, 45.55; H, 5.21; N, 19.32. Found: C, 45.66; H, 5.24; N, 19.28.

(h) [(C<sub>4</sub>CN)<sub>2</sub>im][PF<sub>6</sub>] (5b). The salt 5a (26.67 g, 0.1 mol) was dissolved in water (50 mL), and HPF<sub>6</sub> (60 wt % solution; 24.3 g, 0.10 mol) was added at room temperature. The resulting pale yellow hydrophobic liquid was washed with water (3  $\times$  30 mL). The product was washed with water (3  $\times$  30 mL) and dried under vacuum for 24 h. Yield: 28.2 g, 75%. ESI-MS (H<sub>2</sub>O,  $m/z$ ): positive ion, 231 [(C<sub>4</sub>CN)<sub>2</sub>im]<sup>+</sup>; negative ion, 145 [PF<sub>6</sub>]<sup>-</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  9.08 (s, 1H), 7.81 (s, 2H), 4.45 (t,  $J$ (H,H) = 7.0 Hz, 4H), 2.58 (t,  $J$ (H,H) = 7.0 Hz, 4H), 2.11 (p,  $J$ (H,H) = 7.0 Hz, 4H), 1.74 (p,  $J$ (H,H) = 7.0 Hz, 4H). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>):  $\delta$  136.0, 122.8, 119.4, 48.9, 28.8, 22.0, 15.8. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2247. Anal. Calcd for C<sub>13</sub>H<sub>19</sub>F<sub>6</sub>N<sub>4</sub>P: C, 41.50; H, 5.09; N, 14.89. Found: C, 41.47; H, 5.12; N, 14.92.

(i) [(C<sub>4</sub>CN)<sub>2</sub>im][BF<sub>4</sub>] (5c). The salt 5a (26.67 g, 0.1 mol) and Na[BF<sub>4</sub>] (10.98 g, 0.10 mol) in acetone were stirred at room temperature for 48 h. After filtration and removal of the solvent the resulting pale yellow liquid was washed with THF (3  $\times$  15) and diethyl ether (3  $\times$  30) to give the product. The product was dried under vacuum for 24 h. Yield: 29.90 g, 94%. ESI-MS (methanol,  $m/z$ ): positive ion, 231 [(C<sub>4</sub>CN)<sub>2</sub>im]<sup>+</sup>; negative ion, 87 [BF<sub>4</sub>]<sup>-</sup>. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  8.80 (s, 1H), 7.55 (s, 2H), 4.28 (t,  $J$ (H,H) = 7.0 Hz, 4H), 2.56 (t,  $J$ (H,H) = 7.0 Hz, 4H), 2.03 (p,  $J$ (H,H) = 7.0 Hz, 4H), 1.70 (t,  $J$ (H,H) = 7.0 Hz, 4H). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>):  $\delta$  135.3, 122.5, 121.4, 48.8, 28.4, 21.7, 16.0. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2247. Anal. Calcd for C<sub>13</sub>H<sub>19</sub>BF<sub>4</sub>N<sub>4</sub>: C, 49.08; H, 6.02; N, 17.61. Found: C, 49.01; H, 5.59; N, 17.48.

**Synthesis of Complexes 6a–8a. (a) Typical procedure.** A reaction mixture of PdCl<sub>2</sub> (177 mg, 1.0 mmol) and 1a (373 mg, 2.00 mmol) in 5 mL of acetonitrile was heated at 80 °C for 4 h. After removal of the solvent, the resulting orange solid was washed with dichloromethane (2  $\times$  2 mL) and dried under vacuum to give the product.

(b) [(C<sub>3</sub>CNmim)<sub>2</sub>][PdCl<sub>4</sub>] (6a). Yield: 99%. Mp: 178 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): 9.37 (s, 1H), 7.87 (s, 1H), 7.79 (s, 1H), 4.32 (t,  $J$ (H,H) = 6.8 Hz, 2H), 3.89 (s, 3H), 2.64 (t,  $J$ (H,H) = 6.8 Hz, 2H), 2.18 (m, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): 135.28, 131.36, 120.13, 116.18, 44.02, 31.22, 21.77, 9.99. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2241. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>Cl<sub>4</sub>N<sub>6</sub>Pd: C, 35.03; H, 4.41; N, 15.32. Found: C, 35.07; H, 4.44; N, 15.29.

(c) [(C<sub>3</sub>CNdmmim)<sub>2</sub>][PdCl<sub>4</sub>] (7a). Yield: 96%. Mp: 175 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.72 (s, 1H), 7.68 (s, 1H), 4.22 (t,  $J$ (H,H) = 7.1 Hz, 2H), 3.75 (s, 3H), 2.63 (t,  $J$ (H,H) = 7.1 Hz, 2H), 2.61 (s, 3H), 2.06 (m, 2H). <sup>13</sup>C NMR (DMSO):  $\delta$  148.1, 125.9, 124.2, 123.2, 49.6, 38.2, 28.5, 16.8, 12.7. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2244. Anal. Calcd for C<sub>18</sub>H<sub>28</sub>Cl<sub>4</sub>N<sub>6</sub>Pd: C, 37.49; H, 4.89; N, 14.57. Found: C, 37.52; H, 4.83; N, 14.64.

(d) [(C<sub>3</sub>CN)<sub>2</sub>mim]<sub>2</sub>[PdCl<sub>4</sub>] (8a). Yield: 96%. Mp: 125 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  9.43 (s, 1H), 7.78 (s, 2H), 4.27 (t,  $J$ (H,H) = 7.1 Hz, 2H), 2.61 (p,  $J$ (H,H) = 7.1 Hz, 2H), 2.15 (t,  $J$ (H,H) = 7.1 Hz, 2H). <sup>13</sup>C NMR (DMSO):  $\delta$  137.2, 123.1, 120.1, 48.2, 25.6, 13.5. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2249. Anal. Calcd for C<sub>22</sub>H<sub>30</sub>Cl<sub>4</sub>N<sub>8</sub>Pd: C, 40.36; H, 4.62; N, 17.11. Found: C, 40.40; H, 4.58; N, 17.14.

**Synthesis of Complexes 6b–d and 7b–d. (a) Typical procedure.** A reaction mixture of PdCl<sub>2</sub> (177 mg, 1.0 mmol) and 1b (590 mg, 2.00 mmol) in dichloromethane (5.0 mL) was stirred at room temperature for 4 days. The resulting yellow solid was collected by centrifugation filtration, washed with dichloromethane (2  $\times$  2 mL), and dried under vacuum to give the product.

(b) [(C<sub>3</sub>CNmim)<sub>2</sub>PdCl<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (6b). Yield: 98%. Mp: 130 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): 9.09 (s, 1H), 7.76 (s, 1H), 7.70 (s, 1H),

4.25 (t,  $J$ (H,H) = 7.0 Hz, 2H), 3.85 (s, 3H), 2.58 (t,  $J$ (H,H) = 7.0 Hz, 2H), 2.18 (m, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  135.2, 131.8, 120.1, 116.0, 44.0, 31.1, 21.5, 9.9. <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>): -145 (hept). IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2322. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>Cl<sub>2</sub>F<sub>12</sub>N<sub>6</sub>P<sub>2</sub>-Pd: C, 25.03; H, 3.15; N, 10.95. Found: C, 25.12; H, 3.23; N, 10.88.

(c) [(C<sub>3</sub>CNdmmim)<sub>2</sub>PdCl<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (7b). Yield: 95%. Mp: 160 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.62 (s, 1H), 7.60 (s, 1H), 4.16 (t,  $J$ (H,H) = 7.1 Hz, 2H), 3.72 (s, 3H), 2.56 (s, 3H), 2.53 (t,  $J$ (H,H) = 7.1 Hz, 2H), 2.05 (m, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  = 148.0, 125.9, 124.2, 123.1, 49.6, 38.0, 28.3, 16.8, 12.6. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2324. Anal. Calcd for C<sub>18</sub>H<sub>28</sub>Cl<sub>2</sub>F<sub>12</sub>N<sub>6</sub>P<sub>2</sub>Pd: C, 27.17; H, 3.55; N, 10.56. Found: C, 27.25; H, 3.63; N, 10.64.

(d) [(C<sub>3</sub>CNmim)<sub>2</sub>PdCl<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (6c). Yield: 99%. Mp: 80 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): 9.09 (s, 1H), 7.77 (s, 1H), 7.71 (s, 1H), 4.25 (t,  $J$ (H,H) = 7.00 Hz, 2H), 3.86 (s, 3H), 2.58 (t,  $J$ (H,H) = 7.10 Hz, 2H), 2.18 (m, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  132.1, 120.1, 118.6, 116.0, 44.0, 33.3, 27.8, 9.8. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2324. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>B<sub>2</sub>Cl<sub>2</sub>F<sub>8</sub>N<sub>6</sub>Pd: C, 29.50; H, 3.71; N, 12.90. Found: C, 29.62; H, 3.83; N, 12.88.

(e) [(C<sub>3</sub>CNdmmim)<sub>2</sub>PdCl<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (7c). Yield: 94%. Mp: 130 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.62 (s, 1H), 7.61 (s, 1H), 4.16 (t,  $J$ (H,H) = 7.17 Hz, 2H), 3.72 (s, 3H), 2.57 (s, 3H), 2.56 (t,  $J$ (H,H) = 7.17 Hz, 2H), 2.06 (m, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  148.10, 125.91, 124.20, 123.16, 49.61, 38.09, 28.39, 16.81, 12.60. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2325. Anal. Calcd for C<sub>18</sub>H<sub>28</sub>B<sub>2</sub>Cl<sub>2</sub>F<sub>8</sub>N<sub>6</sub>Pd: C, 31.82; H, 4.15; N, 12.37. Found: C, 31.88; H, 4.14; N, 12.34.

(f) [(C<sub>3</sub>CNmim)<sub>2</sub>PdCl<sub>2</sub>][Tf<sub>2</sub>N]<sub>2</sub> (6d). Yield: 99%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): 9.09 (s, 1H), 7.76 (s, 1H), 7.39 (s, 1H), 4.26 (t,  $J$ (H,H) = 7.00 Hz, 2H), 3.83 (s, 3H), 2.56 (t,  $J$ (H,H) = 7.10 Hz, 2H), 2.14 (m, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  137.2, 124.2, 122.7, 120.0, 48.0, 36.2, 25.6, 13.9. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2315. Anal. Calcd for C<sub>20</sub>H<sub>24</sub>Cl<sub>2</sub>F<sub>12</sub>N<sub>8</sub>O<sub>8</sub>PdS<sub>4</sub>: C, 23.14; H, 2.33; N, 10.79. Found: C, 23.21; H, 2.35; N, 10.78.

(g) [(C<sub>3</sub>CNdmmim)<sub>2</sub>PdCl<sub>2</sub>][Tf<sub>2</sub>N]<sub>2</sub> (7d). Yield: 94%; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.62 (s, 2H), 7.60 (s, 1H), 4.42 (t,  $J$ (H,H) = 7.17 Hz, 2H), 3.72 (s, 3H), 2.96 (s, 3H), 2.65 (t,  $J$ (H,H) = 7.17 Hz, 2H), 2.05 (p, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  145.1, 122.9, 121.5, 120.1, 46.6, 35.1, 25.4, 13.8, 9.6. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2290. Anal. Calcd for C<sub>22</sub>H<sub>28</sub>Cl<sub>2</sub>F<sub>12</sub>N<sub>8</sub>O<sub>8</sub>PdS<sub>4</sub>: C, 24.79; H, 2.65; N, 10.51. Found: C, 24.81; H, 2.62; N, 10.54.

**Synthesis of 9 and 10. (a) Typical Procedure.** PdCl<sub>2</sub> (177 mg, 1.0 mmol) was added to a suspension of 3a in dichloromethane (5.0 mL). The reaction mixture was stirred at room temperature for 5 days, during which time, the orange color of the suspension disappeared and a light yellow suspension formed. The resulting yellow solid was collected by filtration, washed with dichloromethane (2  $\times$  2 mL), and dried under vacuum to give the product.

(b) [(C<sub>3</sub>CNmim)<sub>2</sub>PdCl<sub>2</sub>][PdCl<sub>4</sub>] (9). Yield: 95%. Mp: 153 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  9.11 (s, 1H), 7.77 (s, 1H), 7.71 (s, 1H), 4.24 (t,  $J$ (H,H) = 6.84 Hz, 2H), 3.84 (s, 3H), 2.58 (t,  $J$ (H,H) = 6.80 Hz, 2H), 2.11 (m, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  140.2, 127.1, 125.7, 123.0, 51.0, 39.2, 28.6, 16.9. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2300. Anal. Calcd for C<sub>16</sub>H<sub>24</sub>Cl<sub>6</sub>N<sub>6</sub>Pd<sub>2</sub>: C, 26.47; H, 3.33; N, 11.58. Found: C, 26.51; H, 3.35; N, 11.57.

(c) [(C<sub>3</sub>CNdmmim)<sub>2</sub>PdCl<sub>2</sub>][PdCl<sub>4</sub>] (10). Yield: 94%. Mp: 145 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.23 (s, 1H), 7.18 (s, 1H), 4.06 (t,  $J$ (H,H) = 7.1 Hz, 2H), 3.61 (s, 3H), 2.44 (s, 3H), 2.39 (t,  $J$ (H,H) = 7.1 Hz, 2H), 2.02 (m, 2H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  148.0, 124.6, 122.9, 119.3, 48.7, 37.0, 27.2, 15.8, 11.4. IR (cm<sup>-1</sup>):  $\nu_{\text{C}\equiv\text{N}}$  2309. Anal. Calcd for C<sub>18</sub>H<sub>28</sub>Cl<sub>6</sub>N<sub>6</sub>Pd<sub>2</sub>: C, 28.67; H, 3.74; N, 11.15. Found: C, 28.71; H, 3.68; N, 11.14.

**Synthesis of [(C<sub>3</sub>CN)<sub>2</sub>im]<sub>2</sub>PdCl (11).** A mixture of 8a (6.547 g, 10.0 mmol) and Ag<sub>2</sub>O (1.160 g, 5.0 mmol) was stirred in acetonitrile (50 mL) for 24 h at room temperature with exclusion of light. The resulting mixture was filtered and the yellow filtrate concentrated to ca. 15 mL. Dropwise addition of diethyl ether (50

Table 5. Crystallographic Data for 3a–c, 4a,b, 6a–8a, and 11

	3a	3b	3c	4a	4b	6a	7a	8a	11
formula	C <sub>7</sub> H <sub>7</sub> ClN <sub>4</sub>	C <sub>7</sub> H <sub>7</sub> F <sub>6</sub> N <sub>4</sub> P	(C <sub>7</sub> H <sub>7</sub> BF <sub>4</sub> N <sub>4</sub> ) <sub>2</sub>	C <sub>11</sub> H <sub>15</sub> ClN <sub>4</sub>	C <sub>11</sub> H <sub>15</sub> F <sub>6</sub> N <sub>4</sub> P	C <sub>16</sub> H <sub>24</sub> Cl <sub>4</sub> N <sub>6</sub> Pd	C <sub>18</sub> H <sub>28</sub> Cl <sub>4</sub> N <sub>6</sub> Pd	C <sub>22</sub> H <sub>30</sub> Cl <sub>4</sub> N <sub>8</sub> Pd	C <sub>22</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>8</sub> Pd
fw	182.62	292.14	467.95	238.72	348.24	548.61	576.66	654.74	581.82
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub>	<i>P</i> 1̄	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1̄	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	7.7665(10)	8.2759(13)	5.5750(13)	5.2806(18)	8.2657(8)	14.3813(14)	8.3277(4)	8.3363(7)	11.3577(8)
<i>b</i> (Å)	15.8822(15)	15.020(4)	11.983(3)	11.488(4)	8.9473(6)	10.8029(8)	11.3897(8)	8.8898(6)	9.8994(8)
<i>c</i> (Å)	6.9241(6)	9.024(2)	14.670(2)	10.521(5)	10.6020(10)	14.5861(12)	13.1294(9)	10.6673(11)	12.3556(10)
α (deg)	90	90	90	90	105.391(8)	90	90	90.517(8)	90
β (deg)	91.663(10)	104.332(17)	98.534(16)	98.96(3)	93.605(8)	100.679(13)	104.847(5)	107.260(8)	113.087(7)
γ (deg)	90	90	90	90	94.706(7)	90	90	113.689(7)	90
<i>V</i> (Å <sup>3</sup> )	853.72(16)	1086.8(4)	969.1(3)	630.4(4)	750.48(11)	2226.8(3)	1203.75(13)	683.85(10)	1277.93(17)
<i>Z</i>	4	4	2	2	2	4	2	1	2
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.421	1.785	1.604	1.258	1.541	1.636	1.591	1.590	1.512
<i>μ</i> (mm <sup>-1</sup> )	0.394	0.325	0.155	0.283	0.249	1.327	1.232	1.097	0.961
<i>F</i> (000)	376	584	472	252	356	1104	584	332	592
temp (K)	140(2)	140(2)	293(2)	140(2)	140(2)	140(2)	140(2)	140(2)	210(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
no. of measd rflns	4835	6442	5987	3600	4470	6508	6906	4088	6977
no. of unique rflns	1468	1826	1720	2108	2315	1966	2085	2114	2143
no. of unique rflns ( <i>I</i> > 2σ( <i>I</i> ))	1364	1577	1469	1343	1909	1677	1910	1911	1909
no. of data/ restraints/ params	1468/0/110	1826/0/163	1720/0/145	2108/1/145	2315/0/199	1966/0/125	2085/0/135	2114/0/160	2343/0/151
<i>R</i> <sup>a</sup> ( <i>I</i> > 2σ( <i>I</i> ))	0.0961	0.0713	0.0462	0.0619	0.0410	0.0219	0.0230	0.0245	0.0266
w <i>R</i> <sup>a</sup> (all data)	0.2953	0.2037	0.1221	0.1382	0.1139	0.0494	0.0642	0.0641	0.0693
GOF <sup>b</sup>	1.223	1.064	1.088	0.902	1.086	0.985	1.091	0.992	1.084

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , w*R*2 =  $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ . <sup>b</sup> GOF =  $\{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ , where *n* is the number of data and *p* is the number of parameters refined.

mL) to this solution resulted in the precipitation of a pale yellow solid, which was filtered and washed with diethyl ether (2 × 5 mL) and dried under vacuum to give **11** as a pale yellow solid. Yield: 5.120 g, 88%. <sup>1</sup>H NMR (CD<sub>3</sub>CN): 7.16 (s, 4H), 4.65 (t, *J*(H,H) = 7.0 Hz, 2H), 2.61 (p, *J*(H,H) = 7.0 Hz, 2H), 2.45 (t, *J*(H,H) = 7.0 Hz, 2H). <sup>13</sup>C NMR (CD<sub>3</sub>CN): δ 169.5, 122.0, 120.1, 48.8, 26.2, 14.0. IR (cm<sup>-1</sup>): ν<sub>C=N</sub> 2247. Anal. Calcd for C<sub>22</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>8</sub>Pd: C, 45.41; H, 4.85; N, 19.26. Found: C, 45.40; H, 4.85; N, 19.14.

**Solid-State Structure Determination.** Data collection for the X-ray structure determinations were performed on a KUMA diffractometer system, except for **3b** and **3c**, which were measured on a mar345 IPDS, using graphite-monochromated Mo Kα (0.710 73 Å) radiation. Data reduction was performed by CrysAlis RED.<sup>48</sup> Structure solution and refinement was performed on PCs by using the SHELX97<sup>49</sup> software package, with the exception of **8a**, which was solved with SHELX86. Graphical representations of the structures were made with Diamond.<sup>50</sup> Structures were solved by direct methods (except **3b**, which was solved by Patterson methods) and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against *F*<sup>2</sup>). An empirical absorption correction (DELABS)<sup>51</sup> was applied for **3b,c** and **11**. All atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Compound **8a** was refined using the TWIN command, implemented in SHELX97. Relevant data concerning crystallographic data, data collection, and refinement details are compiled in Table 5.

**Catalysis Procedures. (b) Suzuki Coupling.** In a typical procedure, in a 20 mL two-necked flask fitted with a septum and reflux condenser aryl halide (2.5 mmol, 1 equiv.) was mixed with [C<sub>4</sub>mim][BF<sub>4</sub>] or [C<sub>4</sub>mim][PF<sub>6</sub>] (5 mL) under a nitrogen atmosphere. Next, arylboronic acid (335 mg, 2.75 mmol, 1.1 equiv), Na<sub>2</sub>CO<sub>3</sub> (560 mg, 5.28 mmol, 2.1 equiv) and 2.5 mL of water were

added. Finally, the palladium complex (0.03 mmol, 1.2 mol % based on aryl halide) was added. The mixture was heated to 110 °C and stirred vigorously for 12 h. After reaction the mixture was cooled and the product extracted with diethyl ether. The extracts were washed with brine and water and then dried with MgSO<sub>4</sub>. Biphenyl was obtained by filtering the solution followed by evaporation to dryness. The product was characterized by GC and <sup>1</sup>H NMR. The IL phase was washed with diethyl ether again and placed under vacuum for 18 h prior to reuse. The sample for ICP analysis was prepared by taking 5 mL of diethyl ether extract and evaporated to dryness following addition of 500 mL of 65% HNO<sub>3</sub>. The mixture was stirred at room temperature for 2 days and evaporated to dryness. The remains were dissolved in 15 mL of 2% HNO<sub>3</sub> aqueous solution.

**(b) Heck Reactions.** In a typical procedure, in a 20 mL two-necked flask fitted with a septum and reflux condenser aryl halide (5.0 mmol, 1 equiv) was mixed with [C<sub>4</sub>mim][BF<sub>4</sub>] (5 mL) under a nitrogen atmosphere. Anhydrous sodium acetate (451 mg, 5.5 mmol, 1.1 equiv) and the palladium complex (0.05 mmol, 1–5 mol % of aryl halide) were added. After the flask was flushed with dry nitrogen, ethyl acrylate (0.76 mL, 7.0 mmol, 1.4 equiv) was injected. The mixture was heated to 100 °C and stirred vigorously for 24 h. After reaction the mixture was cooled and the product extracted with ethyl acetate. The combined extracts were washed with brine and water and then dried with MgSO<sub>4</sub>. Biphenyl product was obtained by filtering the solution, followed by evaporation to dryness. The product was characterized by GC and <sup>1</sup>H NMR.

**(c) Stille Reactions.** In a typical procedure, reactions were carried out in a 5 mL two-necked flask fitted with a septum vial under magnetic stirring. To a suspension of palladium complex (0.025 mmol) in IL (1 mL) were added iodobenzene (0.5 mmol) and the tributylvinylstannane (0.6 mmol). The mixture was stirred at 80 °C for 2 h. The products were extracted with *n*-pentane (3 × 1 mL), the organic layers were dried over MgSO<sub>4</sub>, and the product was characterized by GC and <sup>1</sup>H NMR.

**(d) TEM Sample Preparation.** A reaction mixture containing IL and catalyst was taken after the Stille catalysis, and ethanol was added. The mixture was centrifuged, and the nanoparticles were collected at the bottom of the centrifugation vessel. They were then

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suspended in ethanol (2 mL) and centrifuged, and the ethanol was decanted. This process was repeated four times to wash the nanoparticles. Finally, the ethanol/nanoparticle suspension was deposited on a carbon-coated copper grid (500 mesh) and dried at ambient temperature. The TEM images were obtained on a Philips CM 20 transmission electron microscope.

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**Supporting Information Available:** Packing diagrams, text, figures, and a table giving further details of Heck and Stille reactions, including recycling experiments, and CIF files giving X-ray crystallographic data for the structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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