Inorg. Chem. **2004**, *43*, 2197–2205

Synthesis and Characterization of Ionic Liquids Incorporating the Nitrile Functionality

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Received July 10, 2003

A series of imidazolium salts with the nitrile functional group attached to the alkyl side chain, viz. [C_nCNmim][X] (where C_nCNmim is the 1-alkylnitrile-3-methylimidazolium cation and $C_n = (CH_2)_n$, $n = 1–4$; X = Cl, PF_6, and BF_4) and [C_3CNdmim][X] (where C_nCNdmim is the 1-alkylnitrile-2,3-dimethylimidazolium cation and $C_n = (CH_2)_n$, $n = 3$; X = Cl, PF_6, and BF_4), have been prepared and characterized using spectroscopic methods. The majority of the nitrile-functionalized imidazolium salts can be classed as ionic liquids since they melt below 100 °C. Four of the imidazolium salts have been characterized in the solid state using single-crystal X-ray diffraction analysis to reveal an extensive series of hydrogen bonds between H atoms on the cation and the anion. The relationship between the solid-state structure and the melting point is discussed. Key physical properties (density, viscosity, and solubility in common solvents) of the low melting ionic liquid have been determined and are compared with those of the related 1-alkyl-3-methylimidazolium and 1-alkyl-2,3-dimethylimidazolium ionic liquids. It was envisaged that these ionic liquids could act as both solvent and ligand for catalyzed reactions, and this application is demonstrated in hydrogenation reactions, which show that retention of the catalyst in the ionic liquid during product extraction is extremely high.

Introduction

Ionic liquids are currently attracting considerable attention as novel solvents for organic synthesis and catalysis because the chemical industry is under pressure to replace environmentally damaging volatile organic solvents with more benign alternatives.[1] Room temperature ionic liquids (RTILs), especially those based on 1,3-dialkylimidazolium cations, have emerged as leading contenders since they have negligible vapor pressure, are air and moisture stable, and are highly solvating for both ionic and molecular species, and as a result are suitable for multiphasic catalysis.[2] Although applications in synthesis and catalysis have been the most widely explored, with the first industrial scale process now on-line for over a year,[3] ionic liquids are also finding uses in separation processes,[4] in electrochemistry,[5] as electrolytes in solar cells,[6] as lubricants,[7] and as matrixes in MALDI mass spectrometry.[8] Furthermore, the solvent properties of ionic liquids are continually becoming better understood[9] and as such it should be possible to design ionic liquids for particular applications with properties superior to those currently available.

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(1) For reviews see: (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (b) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772. (c) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351.

(2) (a) Gordon, C. M. *Appl. Catal. A: Gen.* **2001**, *222*, 101. (b) Olivier-Bourbigou, H.; Magna, L. *J. Mol. Catal.: A* **2002**, *182−183*, 419. (c) Zhao, D.; Wu, M.; Kou, Y.; Min, E. *Catal. Today* **2002**, *74*, 157. (d) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667.

(3) News of the week in: *Chem. Eng. News* **2003**, March 31, 9.

(4) (a) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis, J. H., Jr.; Rogers, R. D. *Chem. Commun.* **2001**, 135. (b) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, R.; Wierzbicki, A.; Davis Jr. J. H.; Rogers, R. D. *Environ. Sci. Technol.* **2002**, *36*, 2523. (c) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 926.

(5) Demberelnyamba, D.; Shin, B. K.; Lee, H. *Chem. Commun.* **2002**, 1538.

(6) (a) Wang, P.; Zakeeruddin, S. M.; Exnar, I.; Grätzel, M. *Chem. Commun.* **2002**, 2972. (b) Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Grätzel, M. *J. Am. Chem. Soc.* **2003**, *125*, 1166.

(7) (a) Ye, C.; Liu, W.; Chen, Y.; Yu, L. *Chem. Commun.* **2001**, 2244. (b) Li, W. M.; Ye, C. F.; Gong, Q. Y.; Wang H. Z.; Wang, P. *Tribol. Lett.* **2002**, *13*, 81.

(8) (a) Armstrong, D. W.; Zhang, L. K.; He L. F.; Gross, M. L. *Anal. Chem.* **2001**, *73*, 3679. (b) Carda-Broch, S.; Berthod, A.; Armstrong, D. W. *Rapid. Commun. Mass Spectrom.* **2003**, *17*, 553.

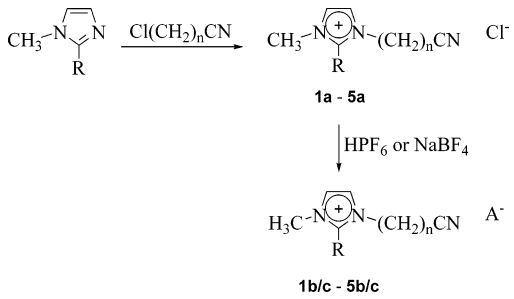
(9) (a) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 14247. (b) Carda-Broch, S.; Berthod, A.; Armstrong, D. W. *Anal. Bioanal. Chem.* **2003**, *375*, 191.

10.1021/ic034801p CCC: $27.50
Published on Web 02/27/2004

One of the attractive features of ionic liquids in synthesis and catalysis is that both the cationic and anionic components can be varied and modified, so that a liquid can be tailored to specific applications. Davis and Rogers have coined the term "task-specific ionic liquids" (TSILs) to describe low melting salts with functional groups, such as amine[4,10] and amide,[11] sulfonic acid,[12] ether and alcohol,[13] carboxylic,[14] urea and thiourea,[15] and phosphine functionalities,[16] as well as fluorous chains[17] attached to the alkyl side chains. The definition of TSILs can be extended to include ionic liquids with functional anions such as carboranes,[18] metal carbonyl anions such as $[Co(CO)_4]^-$ [19] and the Monsanto catalyst $[Rh(CO)_2I_2]^-$,[20] and alkylselenites.[21]

If ionic liquids are to be used to immobilize catalysts in multiphasic reactions, then the design and synthesis of TSILs is extremely important. Many different reactions have been catalyzed using ionic liquids as immobilization solvents including hydrogenation,[22] hydroformylation,[23] and C−C coupling reactions[24] (see ref 2 for reviews of catalyzed reactions in ionic liquids). While the nonnucleophilic nature of many ionic liquids seems to be advantageous, providing a protective environment for the catalyst which can extend its lifetime, it has also emerged that ionic liquids that incorporate a coordination center might be extremely useful, such that the ionic liquid serves as both immobilization solvent and ligand to the catalyst. Wasserscheid et al. first described this concept by introducing a diphenylphosphine group at the 2-position of an imidazolium cation.[25] However, the resulting salt is a not a RTIL and must therefore be dissolved in another ionic liquid for effective use in biphasic catalysis.[26] The ligand, by virtue of being a salt, is highly soluble in ionic liquids and is strongly retained during product extraction. Groups such as NH_2 and OH have also been successfully introduced into the imidazolium cation moieties (see above), but their ability to coordinate to transition metals to give catalytically useful complexes is somewhat limited. More sophisticated functional groups such as thioureas and thioethers have been tethered to imidazolium based ionic liquids, and they have been shown to extract toxic metal ions from aqueous solution.[15]

Scheme 1. Synthesis of Ionic Liquids **1**−**5**[a]



[a] **1a** $n = 1$, R = H; **2a** $n = 2$, R = H; **3a** $n = 3$, R = H; **4a** $n = 4$, R = H; **5a** $n = 3$, R = CH_3; **1b** $n = 1$, R = H, A = PF_6; **1c** $n = 1$, R = H, A = BF_4; **2b** $n = 2$, R = H, A = PF_6; **2c** $n = 2$, R = H, A = BF_4; **3b** $n = 3$, R = H, A = PF_6; **3c** $n = 3$, R = H, A = BF_4; **4b** $n = 4$, R = H, A = PF_6; **4c** $n = 4$, R = H, A = BF_4; **5b** $n = 3$, R = CH_3, A = PF_6; **5c** $n = 3$, R = CH_3, A = BF_4.

This paper describes the synthesis and characterization of imidazolium salts in which a nitrile group is attached to the alkyl side chain. The nitrile group was chosen as it is a promising donor to main group metals such as lithium and potassium and transition metals such as palladium and platinum. We describe the physicochemical properties of these new ionic liquids and show how the length of the alkyl unit linking the imidazolium ring and the CN group influences the melting point of the ionic liquid. In addition, some preliminary data regarding their function in hydrogenation catalysis is provided.

Results and Discussion

The synthetic route used to prepare the 1-alkylnitrile-3-methylimidazolium and 1-alkylnitrile-2,3-dimethylimidazolium salts described herein is depicted in Scheme 1. The imidazolium chlorides $[C_nCNmim][Cl]$ ($C_n = (CH_2)_n$, $n = 1$ **1a**, $n = 2$ **2a**, $n = 3$ **3a**, and $n = 4$ **4a**) are prepared in high yield from 1-methylimidazole and the appropriate chloroalkylnitrile $Cl(CH_2)_nCN$ in a modification to the literature procedure for the related 1-alkyl-3-methylimida-

(10) Herrmann, W. A.; Köcher, C.; Goossen, L. J.; Artus, G. R. J. *Chem.—Eur. J.* **1996**, *2*, 1627.
(11) Lee, K.-M.; Lee, Y.-T.-Y.; Lin, J. B. *J. Mater. Chem.* **2003**, *13*, 1079.
(12) Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, J. H., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 5962.
(13) Branco, L. C.; Rosa, J. N.; Moura Ramos, J. J.; Alfons, C. A. M. *Chem.—Eur. J.* **2002**, *8*, 3671.
(14) (a) Fraga-Dubreuil, J.; Bazureau, J. P. *Tetrahedron Lett.* **2001**, *42*, 6097. (b) Holbrey, J. D.; Reichert, W. M.; Tkatchenko, I.; Bouajila, E.; Walter, O.; Tommasi, I.; Rogers, R. D. *Chem. Commun.* **2003**, 28.
(15) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis Jr., J. H.; Rogers, R. D. *Chem. Commun.* **2001**, 135.
(16) Bronger, R. P. J.; Silva, M. S.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Chem. Commn.* **2002**, 3044.
(17) Merrigan, T. L.; Bates, E. D.; Dorman, S. C.; Davis, J. H., Jr. *Chem. Commun.* **2000**, 2051.
(18) Larsen, A. S.; Holbrey, J. D.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2000**, *122*, 7264.
(19) Brown, R. J. C.; Dyson, J. H.; Ellis, P. J.; Welton, D. J. T. *Chem. Commun.* **2001**, 1862.
(20) Dyson, P. J.; McIndoe, J. S.; Zhao, D. *Chem. Commun.* **2003**, 508.
(21) Sik Kim, H.; Kim, Y. J.; Yong Bae, J.; Joon Kim, S.; Soo Lah, M.; Shik Chin, C. *Organometallics* **2003**, *22*, 2498.
(22) For example, see: (a) Chauvin, Y.; Olivier-Bourbigou, H. *CHEMTECH* **1995**, *25*, 26. (b) Dyson, P. J.; Ellis, D. J.; Parker, D. G.; Welton, T. *Chem. Commun.* **1999**, 25. (c) Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; de Souza, R. F.; Dupont, J. *Polyhedron* **1996**, *15*, 1217. (d) Müller, L. A.; Dupont, J.; de Souza, R. F. *Macromol. Rapid Commun.* **1998**, *19*, 409. (e) Dyson, P. J.; Ellis, D. J.; Welton, T. *Can. J. Chem.* **2001**, *79*, 705. (f) Steines, S.; Wasserscheid, P.; Driessen-Hölscher, B. *J. Prakt. Chem.* **2000**, *342*, 348.
(23) For example, see: (a) Kottsieper, K. W.; Stelzer, O.; Wasserscheid, P. *J. Mol. Catal. A: Chem.* **2001**, *175*, 285. (b) Favre, F.; Olivier-Bourbigou, H.; Commereuc, D.; Saussine, L. *Chem. Commun.* **2001**, 1360. (c) Brasse, C. C.; Englert, U.; Salzer, A.; Waffenschmidt, H.; Wasserscheid, P. *Organometallics* **2000**, *19*, 3818. (d) Sellin, M. F.; Webb, P. B.; Cole-Hamilton, D. J. *Chem. Commun.* **2001**, 781. (e) Stenzel, O.; Raubenheimer, H. G.; Esterhuysen, C. *J. Chem. Soc., Dalton Trans.* **2002**, 1132.
(24) (a) Xu, L.; Chen, W.; Xiao, J. *Organometallics* **2000**, *19*, 1123. (b) Mathews, C. J.; Smith, P. J.; Welton, T.; White, A. J. P.; Williams, D. J. *Organometallics* **2001**, *20*, 3848. (c) Carmichael, A. J.; Earle, M. J.; Holbrey, J. D.; McCormac, P. B.; Seddon, K. R. *Org. Lett.* **1999**, *1*, 997. (d) Mathews, C. J.; Smith, P. J.; Welton, T. *Chem. Commun.* **2000**, 1249. (e) Handy, S. T.; Zhang, X. *Org. Lett.* **2001**, *3*, 233.
(25) Brauer, D. J.; Kottsieper, K.; Liek, C.; Stelzer, O.; Waffenschmidt, H.; Wasserscheid, P. *J. Organomet. Chem.* **2001**, *630*, 177.
(26) (a) Kottsieper, K.; Stelzer, O.; Wasserscheid, P. *J. Mol. Catal.: A* **2001**, *175*, 285. (b) Sirieix, J.; Ossberger, M.; Betzemeier, B.; Knochel, P. *Synlett* **2000**, *11*, 1613.

zolium chlorides.[27] The 1-alkylnitrile-2,3-dimethylimidazolium salt $[C_3CNdimim]Cl$ **5a** is prepared similarly from 1,2-dimethylimidazole and $Cl(CH_2)_3CN$. The synthesis of **1a** has been described previously using an alternative, somewhat more complicated method.[28] The relatively strong electron withdrawing effect of the nitrile group activates chloromethylacetonitrile $ClCH_2CN$ to such an extent that it reacts smoothly with 1-methylimidazole in the absence of solvent to give **1a**. However, as the alkyl chain in the chloroalkylnitrile $Cl(CH_2)_nCN$ precursor increases in length, the temperature required to complete the reaction also increases.

Reaction of **1a**−**4a** with a molecular equivalent of HPF_6 or $NaBF_4$ affords the imidazolium salts $[C_nCNmim][PF_6]$ (n = 1−4) **1b**−**4b** and $[C_nCNmim][BF_4]$ (n = 1−4) **1c**−**4c**, respectively. The imidazolium salts $[C_3CNdimim]PF_6$ **5b** and $[C_3CNdimim]BF_4$ **5c** are prepared from **5a** using an analogous method. For **1b**−**5b** the salts were washed with water in order to remove the hydrogen chloride formed during the anion exchange reaction, whereas THF and diethyl ether were used to wash **1c**−**5c**. The salts were then dried under vacuum for 1−2 days. The salts **2c**, **3c**, **4a**, **4b**, and **3c** are liquid at room temperature and were further purified by filtration through silica and left under vacuum at 40−50 °C for several days. All the imidazolium salts were obtained in medium to high yield. They are stable in air and showed no signs of decomposition up to 150 °C.

The imidazolium salts were characterized using IR, ^{1}H, and ^{13}C NMR spectroscopies, electrospray ionization mass spectrometry (ESI-MS), and elemental analysis. Electrospray ionization mass spectrometry was used to characterize the imidazolium cations diluted in methanol using conditions described previously,[20] and in all cases strong peaks indicative of the parent ion were observed. Aggregates composed of the anions and cations were also observed when the sample was only diluted only moderately, but under high dilution essentially only the parent ions were observed with significant relative intensities. It is worth noting that both the dilution and temperature of the sample influence the extent of ion aggregation.[29] The main feature in the IR spectra is the characteristic C≡N vibrations. The C≡N vibrations decease in wavenumber as the length of the alkyl chain increases, i.e., from 2261 cm^{-1} in **1a** to 2241 cm^{-1} in **4a**, with similar trends for the other salts such that **1** ≫ **2** > **3** ≈ **4** ≈ **5**. The IR spectra exhibit C−H bond stretches between 3150 and 2950 cm^{-1} and weaker C−H bond stretches between 2850 and 2460 cm^{-1}, possibly arising from the formation of hydrogen bonds with the anion. The most noteworthy feature of the ^{1}H NMR spectra of the imidazolium salts is the characteristic resonance for the acidic proton in the 2-position.[30] In compounds **1**−**4** this proton is observed between 9.99 ppm (for **4a**) and 8.45 ppm (for **4b**), but no clear trends are present. It is noteworthy that H−D exchange takes place at the acidic 2-position in all the ionic liquids described, and is fastest for **1a** where the alkyl chain is shortest and the protons interact most strongly with the anion (see below). The alkyl protons adjacent to the nitrile group also exchange with deuterium in **1a**, but at a considerably slower rate.

Table 1. Crystal Data and Details of Structure Determination for **1a**, **3a**, **3b**, and **5b**

	1a	**3a**	**3b**	**5b**
chemical formula	$C_6H_8ClN_3$	$C_8H_{12}ClN_3$	$C_8H_{12}F_6N_3P$	$C_9H_{14}F_6N_3P$
formula weight	157.60	185.66	295.18	309.20
crystal system	orthorhombic	monoclinic	triclinic	triclinic
space group	Pnma	$P2_1/c$	*P-1*	*P-1*
a (Å)	15.0177(17)	8.737(3)	8.022(4)	8.6472(17)
b (Å)	6.2979(7)	11.015(3)	8.161(5)	8.9312(13)
c (Å)	7.8712(5)	10.4099(13)	9.460(2)	9.616(2)
α (deg)	90	90	88.12(3)	74.891(15)
β (deg)	90	102.503(18)	87.01(3)	65.92(2)
γ (deg)	90	90	74.95(5)	78.351(14)
volume (Å^3)	744.46(13)	978.1(4)	597.1(5)	650.7(2)
Z	4	4	2	2
D_{calcd} (g cm^{-3})	1.406	1.261	1.642	1.578
$F(000)$	328	392	300	316
μ (mm^{-1})	0.436	0.342	0.294	0.274
temp (K)	140	140	140	140
wavelength (Å)	0.710 73	0.710 70	0.710 70	0.710 73
measured reflections	4173	5812	3890	3818
unique reflections	689	1720	1985	2017
unique reflections [$I > 2\sigma(I)$]	616	1569	1362	1663
data/parameters	689/61	1720/110	1985/164	2017/173
R^a [$I > 2\sigma(I)$]	0.0273	0.0525	0.0579	0.0501
wR2^a (all data)	0.0753	0.1259	0.1794	0.1467
GOF^b	1.084	1.146	0.990	1.054

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum(w(F_o^2)^2]\}^{1/2}$. ^{b} 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.

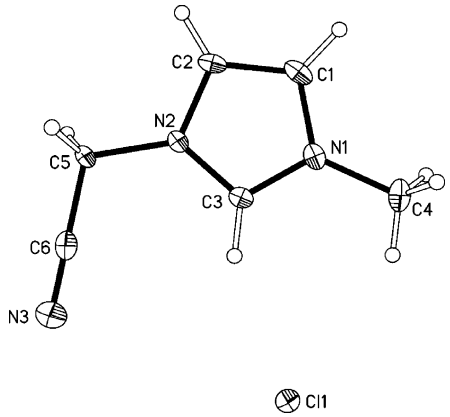


Figure 1. ORTEP representation of the crystal structure of **1a**. Ellipsoids are drawn at the 50% probability level.

Structural Characterization of 1a, 3a, 3b, and 5b in the Solid State. Crystals of suitable for analysis by single-crystal X-ray diffraction were obtained from acetonitrile−diethyl ether solutions at −20 °C. Structural details for the compounds are listed in Table 1, and the structures of **1a**, **3a**, **3b**, and **5b** are illustrated in Figures 1, 2, 3, and 4, respectively, with key bond parameters listed in Table 2 for comparison purposes.

(27) (a) Hitchcock, P. B.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2639. (b) Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; de Souza, R. F.; Dupont, J. *Polyhedron* **1996**, *15*, 1217.
(28) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *Organometallics* **1998**, *17*, 2162.
(29) Dyson, P. J.; McIndoe, J. S. *Inorg. Chim. Acta* **2003**, *354*, 68.
(30) Seddon, K. R.; Stark, A.; Torres, M. J. *Pure Appl. Chem.* **2000**, *72*, 2275.

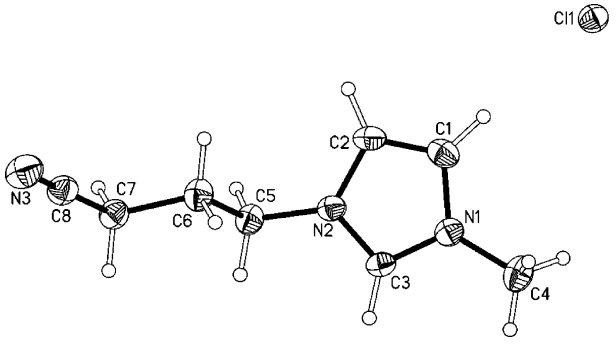


Figure 2. ORTEP representation of the crystal structure of **3a**. Ellipsoids are drawn at the 50% probability level.

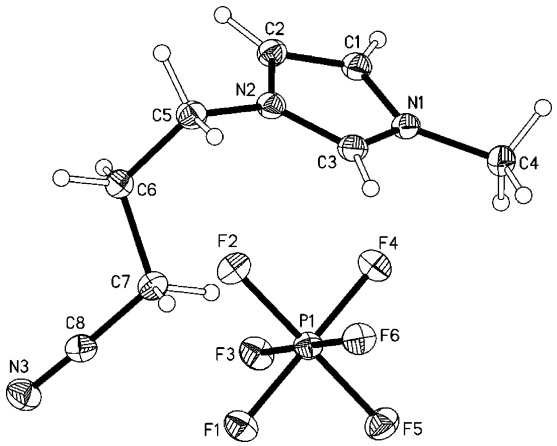


Figure 3. ORTEP representation of the crystal structure of **3b**. Ellipsoids are drawn at the 50% probability level.

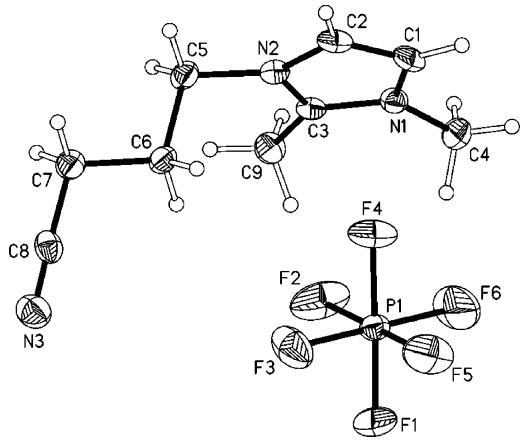


Figure 4. ORTEP representation of the crystal structure of **5b**. Ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) for **1a**, **3a**, **3b**, and **5b**

	1a	3a	3b	5b
N1−C1	1.384(3)	1.377(2)	1.377(4)	1.392(3)
C1−C2	1.361(3)	1.349(3)	1.350(5)	1.349(3)
C2−N2	1.377(3)	1.379(2)	1.392(5)	1.387(3)
N2−C3	1.348(3)	1.334(2)	1.320(4)	1.356(3)
C3−N1	1.336(3)	1.331(2)	1.322(5)	1.358(3)
N1−C4	1.478(3)	1.462(2)	1.470(4)	1.473(3)
N2−C5	1.477(3)	1.461(2)	1.469(5)	1.486(3)

In the solid-state structures of **1a**, **3a**, **3b** and **5b** the parameters of the atoms in the side chains are generally very close despite the differences of their lengths and the presence of different anions. The C≡N bond lengths are also essentially the same [1.139(5)−1.149(3) Å] in the four compounds. The imidazolium rings are all planar; however, slight differences between the imidazolium rings can be appreciated by a comparison of **1a** with **3a**. The distances of the N2−C5 and N2−C3 bonds in **1a** [1.477(3) and 1.348(3) Å] are both slightly longer than in **3a** [1.461(2) and 1.334(2) Å]. More significant is the difference of the C═C bond lengths. In **1a**, the value is 1.361(3) Å, while in **3a** the value of 1.348(3) Å—remarkably shorter! The N2−C2 distance in **3a** [1.379(2) Å] is significantly shorter than that in **3b** [1.392(5) Å], while the N2−C3 bond in **3a** [1.334(2) Å] is significantly longer than it is in **3b** [1.320(4) Å]. Slight changes in **5b** at the C3-position, compared to **3a** and **3b** [mean 1.36 Å versus 1.33 and 1.32 Å] may be attributed to the presence of the methyl group in **5b**; both the N1−C3 and N2−C3 distances are longer than they are in **3a** and **3b**, and as a result, **5b** shows the smallest N1−C3−N2 angle [**3a**, 108.19(15)°; **3b**, 109.9(3)°; **5b**, 106.5(2)°].

It is possible that the slight differences in the molecular geometry are caused by the different hydrogen bond networks arising from the different anions and different side chains. Hydrogen bonds in imidazolium salts have been a focus of many reports including NMR studies[31] and single-crystal X-ray analysis.[32] Hydrogen bonds between the hydrogen bond acceptor usually from the counteranions and the H atoms in the imidazolium ring are the most frequently observed interactions, and in most cases they are the strongest. However, the strength of the hydrogen bond is largely dependent on the nature of the counteranion. In many cases, only a small variation in the molecular structure will give rise to significant changes in the crystal structure.[33] The introduction of the CN group in the side chain of the ionic liquid completely changes the architecture of the hydrogen bonding network. For **1a**, **3a**, and **3b** the hydrogen atom at the 2-position of the imidazolium ring forms one of the strongest (shortest) C−H···X (X = Cl, F) hydrogen bonds which occur in the solid state [**1a**, H3···Cl1, 2.49 Å; **3a**, H3···Cl1, 2.71 Å; **3b**, H3···F1, 2.43 Å]. Other weaker (longer) C−H···X interactions involve the remaining hydrogens of the imidazolium and the methylene hydrogens of the side chains. Interactions between the π-system and the anions also appear to be important in certain structures (see Figure 5). In the case of compound **3a** the chloride anion is surrounded by hydrogens and it does not interact with the π-system of the imidazolium ring; instead, it interacts with the nitrile function [3.102 Å]. However, in **3b** and **5b** the larger hexafluorophosphate interacts with the π-system [**3b**, F2···ring, 3.297 Å; **5b**, F4···ring, 3.131 Å]. This may explain why in these two cases no interactions occur with the terminal CN group. If the side chain is smaller as in **1a**, CN moieties may have weak hydrogen bond interactions [H2···N3,

(31) Huang, J.-F.; Chen, P.-Y.; Sun, I.-W.; Wang, S. P. *Inorg. Chim. Acta* **2000**, *320*, 7.
(32) (a) Avent, A. G.; Chaloner, P. A.; Day, M. P.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans*. **1994**, 3405. (b) Elaiwi, A.; Hitchcock, P. B.; Seddon, K. R.; Srinivasan, N.; Tan, Y.-M.; Welton, T.; Zora, J. A. *J. Chem. Soc., Dalton Trans*. **1995**, 3467.
(33) Dupont, J.; Suarez, P. A. Z.; de Souza, R. F.; Burrow, R. A.; Kintzinger, J.-P. *Chem.—Eur. J.* **2000**, *6*, 2377.

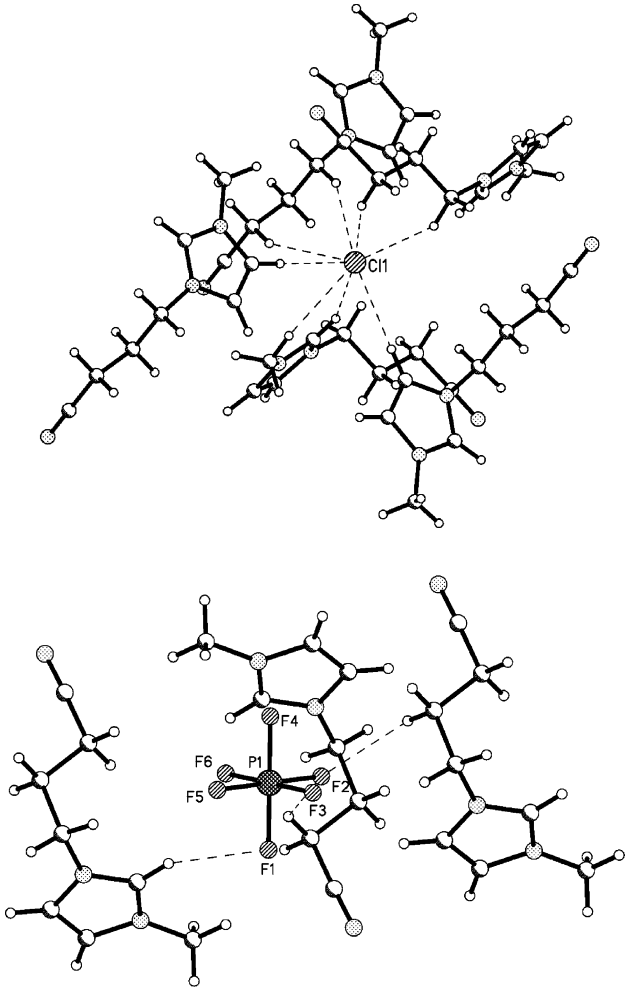


Figure 5. Anion−cation interactions for (top) **3a** and (bottom) **3b** showing the C−H···X interactions around the two different anions.

2.56 Å]. Presumably the interaction of the π-system with the anion is weaker than conventional hydrogen bonds, and since it reduces the number of hydrogen bonds between the anion and cation the melting point is also lowered.

Overall, the extent of intermolecular hydrogen bonding revealed from the solid-state structural studies indicates that these ionic liquids can be described as polymeric supermolecular networks. Such a view is in keeping with previous observations.[34]

Physical Properties of the Ionic Liquids. The relationship between molecular structure and melting point of ionic liquids has been investigated previously,[35] and from a theoretical perspective, the melting point is determined by the strength of a crystal lattice, which in turn is controlled by three main factors, viz. intermolecular forces, molecular symmetry, and the conformational degrees of the freedom of a molecule.[36] Unlike hydrogen bond free molecules, of

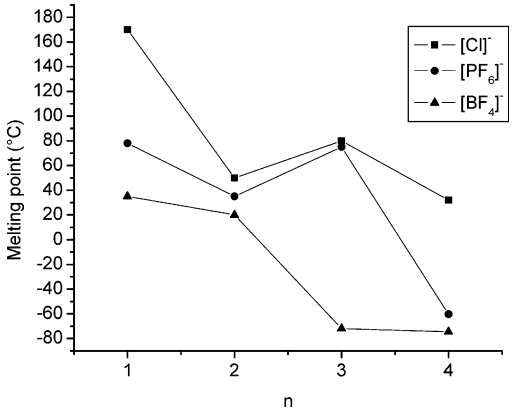


Figure 6. Melting point data for **1**−**4**.

which the melting points are somewhat predictable using different approaches,[37] the melting points of imidazolium salts are more complicated and less predictable. It has been suggested that packing inefficiency and disorder are key factors in keeping some imidazolium salts as low-temperature liquids.[38] However, the exact reason many imidazolium salts are low melting liquids remains unknown, and only slight variations in the molecular structure may result in very different crystal structures, which in turn leads to very different physical properties. It is also well-known that impurities in ionic liquids, notably residual chloride, strongly influence the physical properties of ionic liquids;[30,39] therefore we tested for the presence of chloride using $AgNO_3$, and in all cases chloride was not detected.

A graph showing how the melting points of compounds **1**−**4** vary is presented in Figure 6. Of the 15 nitrile-functionalized imidazolium salts reported, only four salts have melting points above 100 °C, which by the most widely used definition do not constitute ionic liquids.[1c] The salts **2c**, **3c**, **4a**, **4b**, and **3c** are liquid around room temperature, and of these three have very low melting points (−60 °C and below). From Figure 6 it is clear that both the anion and the cation significantly influence the melting point of the imidazolium salt. For each cation, the melting point follows the trend Cl > PF_6 > BF_4, which is in keeping with related salts with alkyl-substituted imidazolium cations.

From Figure 6 it is also clear that the length of the alkyl group also strongly influences the melting point, with the longer more flexible groups resulting in lower melting points. Again, such a trend has been observed previously with related salts, although as the alkyl chain increases beyond a certain length the melting point begins to increase.[40] Both **3b** and **3c** have higher melting points than the unfunctionalized analogues [C_4mim][PF_6] and [C_4mim][BF_4] (C_4mim = 1-butyl-3-methylimidazolium). The increased melting point could be due to the more rigid nature of the cation imposed by the CN group and/or due to the possibility of increased

(34) (a) Wadhawan, J. D.; Schröder, W.; Neudeck, A.; Wilkins, S. J.; Compton, R. G.; Marken, F.; Consorti, C. S.; de Souza, R. F.; Dupont, J. *J. Electronal. Chem.* **2000**, *493*, 75. (b) Schröder, W.; Wadhawan, J. D.; Compton, R. G.; Marken, F.; Suarez, P. A. Z.; Consorti, C. S.; de Souza, R. F.; Dupont, J. *New J. Chem*. **2000**, *24*, 1009.
(35) Katritzky, A. R.; Jain, R.; Lomaka, A.; Petrukhin, R.; Maran, U.; Karelson, M. *Cryst. Growth Des.* **2001**, *1*, 261.
(36) Dearden, J. C. *Sci. Total Environ.* **1991**, *109/110*, 59.
(37) Lyman, W. J.; Reehl, W. F. In *Handbook of Chemical Property Estimation Methods*; Rosenblatt, D. H., Ed.; McGraw-Hill: New York, 1982.
(38) Larsen, A. S.; Holbrey, J. D.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **2000**, *122*, 7264.
(39) Suarez, P. A. Z.; Einloft, S.; Dullius, J. E. L.; de Souza, R. F.; Dupont, J. *J. Chim. Phys*. **1998**, *95*, 1626.

Table 3. Density, Viscosity, and Solubility Data of the Room Temperature Ionic Liquids

ionic liquid	density[a] (g·mL^{-1})	viscosity[b] (mPa·s)	solubility in common solvents				
			H_2O	Et_2O	EtOH	acetone	hexane
[C_2CNmim][BF_4] **2c**	2.15	65.5	miscible	immiscible	miscible	miscible	immiscible
[C_3CNmim][BF_4] **3c**	1.87	230	miscible	immiscible	immiscible	miscible	immiscible
[C_4CNmim][Cl] **4a**	1.61	5222	miscible	immiscible	miscible	immiscible	immiscible
[C_4CNmim][PF_6] **4b**	1.99	2181	partly miscible	immiscible	immiscible	miscible	immiscible
[C_4CNmim][BF_4] **4c**	1.71	552.9	miscible	immiscible	immiscible	miscible	immiscible
[C_4mim][PF_6]	1.37	320.3[c]	partly miscible	immiscible	partly miscible	miscible	immiscible
[C_4mim][BF_4]	1.14	115.2[d]	miscible	immiscible	immiscible	miscible	immiscible

[a] Determined at 20 °C. [b] Determined at 25 °C. [c] Literature values 308.3 (at 20 °C)[30] and 371.0 (at 20 °C).[13] [d] Literature values 154.0 (at 20 °C)[30] and 104.9 (at 20 °C).[13]

hydrogen bonding interactions (see above). In general, replacement of the proton in the 2-positon by a methyl group increases the melting point of the salt,[41] and as expected, [C_3CNdimim]Cl **5a** has a higher melting point than [C_3CNmim]Cl **3a** (105 versus 80 °C).

The density, viscosity, and solubility data of the five salts that are liquid at ambient temperature are listed in Table 3, together with the related data for [C_4mim][PF_6] and [C_4mim][BF_4] for comparison purposes.

The density of the nitrile-functionalized ionic liquid deceases as the alkyl chain increases in length. For example, a comparison of the densities of the tetrafluoroborate salts shows a decrease in the order **2c** (2.15 g·mL^{-1}) > **3c** (1.87 g·mL^{-1}) > **4c** (1.71 g·mL^{-1}). In all cases the densities of the alkylnitrile ionic liquids are higher than those of the nonfunctionalized analogues. Incorporating the nitrile group serves to increase the density of the ionic liquid, which may result in improved separation with other solvents when used in biphasic catalysis.

It has been shown that the viscosity of imidazolium salts is influenced by their hydrogen bonding ability and by the strength of their van der Waals interactions, which in turn is strongly dependent on the type of anion present.[41] The viscosity of the ionic liquids varies considerably, and while it is not easy to draw any firm conclusions, it would appear from the three tetrafluoroborate salts examined that there is a steady increase in viscosity with the length of the alkyl chain, presumably as a result of the increased van der Waals interactions.

The solubility data of the new ionic liquids is similar to that of the related nonfunctionalized ionic liquids [C_4mim][PF_6] and [C_4mim][BF_4] (see Table 3). The new ionic liquids are immiscible with nonpolar solvents such as diethyl ether and hexane, whereas with polar solvents such as ethanol and acetone the solubility depends on the anion as has been described elsewhere.

Preliminary Evaluation as Immobilization Media in Hydrogenation Catalysis. As mentioned above, it was envisaged that the nitrile derivatized ionic liquids might be good solvents for multiphasic catalysis, at least in terms of catalyst retention and product separation. Dissolution of $PdCl_2$ in [C_3CNmim][BF_4] **3c** affords [Pd(NCC_3mim)$_2Cl_2$][BF_4]$_2$ in quantitative yield. The resulting solution was used to hydrogenate 1,3,-cyclohexadiene under biphasic conditions, which afforded cyclohexene and cyclohexane. The overall conversion was 90% and the turnover frequency was 247 mol mol^{-1} h^{-1}. Cyclohexene was formed with a selectivtiy of 97%, possibly because the monoene dissociates from the catalyst and is less soluble in the ionic liquid than the diene, which is therefore hydrogenated in preference. Hydrogenation reactions have been widely studied in ionic liquids,[22] including the substrate 1,3-cyclohexadiene,[42] and ionic liquids have been shown to be well suited to the partial reduction of cyclohexane to cyclohexene.[43] It is clearly an advantage that the ionic liquids system gives such selectivy, ascribed to the higher solubility of the cyclohexadiene substrate in the ionic liquid relative to the cyclohexene product, which is automatically removed from the reaction medium. However, the most important feature of the system described herein is that the catalyst is part of the ionic liquid and therefore not easily lost during extraction of the product. No decrease in activity is observed after reuse of the catalyst solution, and using inductively coupled plasma analysis, we were unable to detect any palladium residues in the organic phase.

Experimental Section

The 1-methylimidazole and 1,2-dimethylimidazole and chloroakylnitrile were purchased from Fluka. HPF_6 and $NaBF_4$ were purchased from Aldrich and were used as received without further purification. The synthesis of the imidazolium salts **1a**−**5a** was performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques in solvents dried using the appropriate reagents and distilled prior to use. All other compounds were made without precautions to exclude air or moisture. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. NMR spectra were measured on a Bruker DMX 400, using $SiMe_4$ for ^{1}H and 85% H_3PO_4 for ^{31}P as external standards at 20 °C. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca

(40) Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc., Dalton Trans*. **1999**, 2133.
(41) Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem*. **1996**, *35*, 1168.
(42) (a) Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 4228. (b) Huang, J.; Jiang, T.; Gao, H.; Chang, Y.; Zhao, G.; Wu, W. *Chem. Commun*. **2003**, 1654.
(43) (a) Parshall, G. W. *J. Am. Soc. Chem*. **1972**, *94*, 8716. (b) Chauvin, Y.; Mussmann, L.; Olivier, H. *Angew. Chem., Int. Ed. Engl*. **1996**, *34*, 2698. (c) Dupont, J.; Suarez, P. A. Z.; Umpierre, A. P.; de Souza, R. F. *J. Braz. Chem. Soc*. **2000**, *11*, 293. (d) Consorti, C. S.; Umpierre, A. P.; de Souza, R. F.; Dupont, J.; Suarez, P. A. Z. *J. Braz. Chem. Soc*. **2003**, *14*, 401.

XP Plus quadrupole ion trap instrument on sample diluted in methanol.[20] Samples were infused directly into the source at 5 μL min^{-1} using a syringe pump, the spray voltage was set at 5 kV, and the capillary temperature was set at 50 °C. Elemental analysis was carried out at the Institute of Molecular and Biological Chemistry at the EPFL. Samples **2c**, **3c**, **4a**, **4b**, and **4c** were purified by filtration through silica and left under vacuum (ca. 0.1 mmHg) at 40−50 °C to remove traces of salt impurities and volatile components. Differential scanning calorimetry was performed with a SETARAM DSC 131. Density was determined with a pycometer at room temperature (20 ± 1 °C) on 1.0 mL of sample. The measurements were repeated three times and average values were used. Viscosities were measured with a Brookfield DV-II+ viscometer on 0.50 mL of sample. The temperature of the samples was maintained to 25 ± 1 °C by means of an external temperature controller. The measurements were performed in duplicate.

Synthesis of [CCNmim]Cl 1a. A mixture of 1-methylimidazole (8.21 g, 0.10 mol) and $ClCH_2CN$ (9.06 g, 0.12 mol) was stirred at room temperature (RT) for 24 h, during which time the reaction mixture turned into a solid. The solid was washed with diethyl ether (3 × 30 mL) and dried under vacuum for 24 h. Yield: 14.5 g, 92%; mp 170 °C. Crystals suitable for X-ray diffraction were obtained by slow diffusion of ethyl ether into an acetonitrile solution of the compound at RT. ESI-MS (CH_3OH): positive ion, 122 [CCNmim]; negative ion, 35 [Cl]. ^{1}H NMR (D_2O): δ = 9.06 (s, 1H), 7.72 (s, 1H), 7.61 (s, 1H), 4.65 (s, 2H), 3.96 (s, 3H). ^{13}C NMR (D_2O): δ = 140.40, 127.65, 125.52, 117.02, 74.82, 39.54. IR (cm^{-1}): 3177, 3126, 3033 (ν_{C-H} aromatic), 2979, 2909, 2838, 2771 (ν_{C-H} aliphatic), 2261 ($\nu_{C\equiv N}$), 1769 ($\nu_{C=N}$). Anal. Calcd for $C_6H_8ClN_3$ (%): C 45.73, H 5.12, N 22.66. Found: C 45.86, H 5.26, N 22.58.

Synthesis of [CCNmim]PF_6 1b. To a solution of **1a** (4.73 g, 0.03 mol) in water (50 mL), HPF_6 (8.03 g, 60 wt %, 0.033 mol) was added at RT. After 10 min the solid that had formed was collected by filtration and washed with ice−water (3 × 15 mL) and then dried under vacuum. Yield: 5.61 g, 70%; mp 78 °C. ESI-MS (CH_3OH): positive ion, 122 [CCNmim]; negative ion, 145 [PF_6]. ^{1}H NMR (CD_3CN): δ = 8.59 (s, 1H), 7.53 (s, 1H), 7.44 (s, 1H), 5.41 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (CD_3CN): δ = 139.9, 127.6, 125.5, 120.5, 40.0, 39.3. ^{31}P NMR (CD_3CN): −145.25 (hept). IR (cm^{-1}): 3180, 3133, 3027 (ν_{C-H} aromatic), 2983, 2938 (ν_{C-H} aliphatic), 2274 ($\nu_{C\equiv N}$), 1602 ($\nu_{C=N}$). Anal. Calcd for $C_6H_8N_3F_6P$ (%): C 26.98, H 3.02, N 15.73. Found: C 27.02, H 3.09, N 15.66.

Synthesis of [CCNmim]BF_4 1c. A mixture of **1a** (4.73 g, 0.03 mol) and $NaBF_4$ (3.62 g, 0.033 mol) in acetone (80 mL) was stirred at room temperature for 48 h. After filtration and removal of the solvents the resulting pale yellow waxy solid was washed with THF and diethyl ether to give the product. Yield: 5.76 g, 92%; mp 35 °C. ESI-MS (CH_3OH): positive ion, 122 [CCNmim]; negative ion, 87 [BF_4]. ^{1}H NMR (CD_3CN): δ = 8.67 (s, 1H), 7.56 (s, 1H), 7.47 (s, 1H), 5.26 (s, 2H), 3.87 (s, 3H). ^{13}C NMR ($CDCl_3$): δ = 140.35, 127.57, 125.46, 116.76, 39.79, 39.21. IR (cm^{-1}): 3171, 3124, 3015 (ν_{C-H} aromatic), 2977, 2845 (ν_{C-H} aliphatic), 2253 ($\nu_{C\equiv N}$), 1588 ($\nu_{C=N}$). Anal. Calcd for $C_6H_8BF_4N_3$(%): C 34.48, H 3.86, N 20.11. Found: C 34.52, H 3.82, N 20.26.

Synthesis of [C_2CNmim]Cl 2a. A mixture of 1-methylimidazole (8.21 g, 0.10 mmol) and $Cl(CH_2)_2CN$ (10.74 g, 0.12 mol) was stirred in toluene (20 mL) at 70 °C for 24 h. The resulting white solid was washed with diethyl ether (5 × 30 mL). The product was then dried in a vacuum for 24 h. Yield: 15.5 g, 82%; mp 50 °C. ESI-MS (CH_3OH): positive ion, 136 [C_2CNmim]; negative ion, 35 [Cl]. ^{1}H NMR (D_2O): δ = 8.73 (s, 1H), 7.48 (s, 1H), 7.46 (s, 1H), 4.64 (t, J(H,H) = 6.8 Hz, 2H), 3.94 (s, 3H), 3.03 (t, J(H,H) = 6.8 Hz, 2H); ^{13}C NMR (D_2O): δ = 139.58, 138.05, 126.16, 122.53, 47.86, 42.12, 38.83. IR (cm^{-1}): 3244 (ν_{C-H} aromatic), 2916, 2788, 2700 (ν_{C-H} aliphatic), 2250 ($\nu_{C\equiv N}$), 1720 ($\nu_{C=N}$). Anal. Calcd for $C_7H_{10}ClN_3$ (%): C 48.99, H 5.87, N 24.48. Found: C 50.02, H 5.75, N 24.71.

Synthesis of [C_2CNmim]PF_6 2b. The same procedure as that described above for **1b** was followed, except **2a** (5.15 g, 0.03 mol) and HPF_6 (8.03 g, 60 wt %, 0.033 mol) were used, and the product was obtained as a white solid. Yield: 6.83 g, 81%; mp 35 °C. ESI-MS (CH_3OH): positive ion, 136 [C_2CNmim]; negative ion, 145 [PF_6]. ^{1}H NMR (CD_3CN): δ = 8.64 (s, 1H) 7.50 (s, 1H), 7.43 (s, 1H), 4.46 (t, J(H,H) = 6.49 Hz, 2H), 3.89 (s, 3H), 3.03 (t, J(H,H) = 6.49 Hz, 2H). ^{13}C NMR (CD_3CN): δ = 139.36, 127.13, 125.34, 120.49, 47.87, 39.01, 21.92. ^{31}P NMR (CD_3CN): −142.90 (hept). IR (cm^{-1}): 3168, 3126, 3101 (ν_{C-H} aromatic), 2964 (ν_{C-H} aliphatic), 2255 ($\nu_{C\equiv N}$), 1704 ($\nu_{C=N}$). Anal. Calcd for $C_7H_{10}F_6N_3P$ (%): C 29.90, H 3.58, N 14.95. Found: C 29.95, H 3.62, N 14.88.

Synthesis of [C_2CNmim]BF_4 2c. The same procedure as that described above for **1c** was followed, except **2a** (5.15 g, 0.03 mol) was used instead of **1a**. The product was obtained as pale yellow liquid at room temperature. Yield: 5.69 g, 85%; mp 20 °C. ESI-MS (CH_3OH): positive ion, 136 [C_2CNmim]; negative ion, 87 [BF_4]. ^{1}H NMR (CD_3CN,): δ = 8.56 (s, 1H), 7.41 (s, 1H), 7.37 (s, 1H), 4.48 (brs, 2H), 3.88 (s, 3H), 3.05 (brs, 2H). ^{13}C NMR (CD_3CN): δ = 138.33, 126.22, 122.56, 121.04, 47.81, 38.54, 21.81. IR (cm^{-1}): 3165 and 3124 (ν_{C-H} aromatic), 2955 and 2855 (ν_{C-H} aliphatic), 2251 ($\nu_{C\equiv N}$), 1736 ($\nu_{C=N}$). Anal. Calcd for $C_7H_{10}N_3BF_4$ (%): C 37.70, H 4.52, N 18.84. Found: C 37.52, H 4.65, N 19.05.

Synthesis of [C_3CNmim]Cl 3a. A mixture of 1-methylimidazole (8.21 g, 0.10 mmol) and $Cl(CH_2)_3CN$ (12.43 g, 0.12 mol) was stirred at 80 °C for 24 h. The resulting white solid was washed with diethyl ether (3 × 30 mL). The product was dried in a vacuum for 24 h. Yield: 17.6 g, 95%; mp 80 °C. ESI-MS (CH_3OH): positive ion, 150 [C_3CNmim]; negative ion, 35 [Cl]. ^{1}H NMR ($CDCl_3$): δ = 8.73 (s, 1H), 7.45 (s, 1H), 7.39 (s, 1H), 4.27 (t, J(H,H) = 6.8 Hz, 2H), 3.82 (s, 3H), 2.50 (t, J(H,H) = 6.8 Hz, 2H), 2.20 (t, J(H,H) = 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ = 134.11, 130.49, 120.01, 116.19, 44.01, 30.87, 21.21, 9.87. IR (cm^{-1}): 3373, 3244, 3055 (ν_{C-H} aromatic), 3029, 2974, 2949, 2927 (ν_{C-H} aliphatic), 2243 ($\nu_{C\equiv N}$), 1692 ($\nu_{C=N}$). Anal. Calcd for $C_8H_{12}ClN_3$ (%): C, 51.76, H, 6.51, N, 22.63. Found: C 51.72, H 6.55, N 22.71.

Synthesis of [C_3CNmim]PF_6 3b. The same procedure as that described above for **1b** was followed, except **3a** (5.57 g, 0.03 mol) was used instead of **1a**. The product was obtained as white solid. Yield: 6.90 g, 78%; mp 75 °C. ESI-MS (CH_3OH): positive ion, 150 [C_3CNmim]; negative ion, 145 [PF_6]. ^{1}H NMR ($CDCl_3$): δ = 8.63 (s, 1H), 7.59 (s, 1H), 7.55 (s, 1H), 4.42 (t, J(H,H) = 7.0 Hz, 2H), 4.03 (s, 3H), 2.66 (t, J(H,H) = 7.0 Hz, 2H), 2.33 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 135.50, 131.80, 120.10, 116.50, 44.25, 33.30, 22.50, 9.98. ^{31}P NMR ($CDCl_3$): −145.90 (hept). IR (cm^{-1}): 3171, 3158, 3128 (ν_{C-H} aromatic), 2980, 2807 (ν_{C-H} aliphatic), 2246 ($\nu_{C\equiv N}$), 1696 (($\nu_{C=N}$). Anal. Calcd for $C_8H_{12}F_6N_3P$ (%): C 32.55, H 4.10, N 14.24. Found: C 32.59, H 4.11, N 14.30.

Synthesis of [C_3CNmim]BF_4 3c. The same procedure as that described above for **1c** was followed, except **3a** (5.57 g, 0.03 mol) was used instead of **1a**. Yield: 6.4 g, 90%; mp −71.9 °C. ESI-MS (CH_3OH): positive ion, 150 [C_3CNmim]; negative ion, 87 [BF_4]. ^{1}H NMR ($CDCl_3$): δ = 9.32 (s, 1H), 8.18 (s, 1H), 8.14 (s, 1H), 4.96 (brs, 2H), 4.54 (s, 3H), 3.20 (brs, 2H), 2.85 (brs, 2H). ^{13}C NMR ($CDCl_3$): δ = 135.03, 131.17, 120.69, 116.71, 44.69, 33.78,

22.01, 10.15. IR (cm^{-1}): 3161, 3121 (ν_{C-H} aromatic), 2971 (ν_{C-H} aliphatic), 2249 ($\nu_{C\equiv N}$), 1712 ($\nu_{C=N}$). Anal. Calcd for $C_8F_4BH_{12}N_3$ (%): C 40.54, H 5.10, N 17.73. Found: C 40.58, H 5.13, N 17.69.

Synthesis of [C_4CNmim]Cl 4a. A mixture of 1-methylimidazole (8.21 g, 0.10 mmol) and $Cl(CH_2)_4CN$ (14.1 g, 0.12 mol) was stirred at 80 °C for 4 h. The temperature was then increased to 110 °C, and the reaction mixture was stirred for a further 2 h. After cooling, the reaction mixture was washed with diethyl ether (3 × 15 mL) and dried under vacuum for 24 h. The product was obtained as viscous brownish liquid. Yield: 17.9 g, 90%; mp 32 °C. ESI-MS (CH_3OH): positive ion, 164 [C_4CNmim]; negative ion, 35 [Cl]. ^{1}H NMR (CD_3CN): δ = 9.99 (s, 1H), 7.75 (s, 1H), 7.70 (s, 1H), 4.41 (t, J(H,H) = 7.2 Hz, 2H), 3.94 (s, 3H), 2.57 (t, J(H,H) = 7.0 Hz, 2H), 2.07 (m, J(H,H) = 6.8 Hz, 2H), 1.64 (m, J(H,H) = 6.8 Hz, 2H). ^{13}C NMR (CD_3CN): δ = 134.22, 129.29, 127.97, 125.81, 123.18, 41.50, 34.43, 27.47, 21.77. IR (cm^{-1}): 3138, 3088, 3082 (ν_{C-H} aromatic), 2948 (ν_{C-H} aliphatic), 2241 ($\nu_{C\equiv N}$), 1701 (($\nu_{C=N}$). Anal. Calcd for $C_9H_{14}ClN_3$ (%): C 54.13, H 7.07, N, 21.04. Found: C 54.21, H 7.09, N, 21.09.

Synthesis of [C_4CNmim]PF_6 4b. The same procedure as that described above for **1b** was followed, except **4a** (5.99 g, 0.03 mol) was used instead of **1a**. The product was obtained as brown liquid at room temperature. Yield: 7.6 g, 82%; mp −60.3 °C. ESI-MS (CH_3OH): positive ion, 164 [C_3CNmim]; negative ion, 145 [PF_6]. ^{1}H NMR (CD_3CN): δ = 8.45 (s, 1H), 7.38 (s, 1H), 7.35 (s, 1H), 4.15 (t, J(H,H) = 7.17 Hz, 2H), 3.83 (s, 3H), 2.44 (t, J(H,H) = 7.17 Hz, 2H), 1.93 (m, J(H,H) = 7.17, 2H), 1.64 (m, J(H,H) = 7.17, 2H). ^{13}C NMR (CD_3CN): δ = 138.95, 126.72, 125.16, 122.85, 120.80, 38.78, 31.61, 24.74, 18.93. ^{31}P NMR ($CDCl_3$): −140.80 (hept). IR (cm^{-1}): 3168, 3123 (ν_{C-H} aromatic), 2972, 2901 (ν_{C-H} aliphatic), 2250 ($\nu_{C\equiv N}$), 1577 ($\nu_{C=N}$). Anal. Calcd for $C_9F_6H_{14}N_3P$ (%): C 34.96, H 4.56, N 13.59. Found: C 35.05, H 4.41, N 13.64.

Synthesis of [C_4CNmim]BF_4 4c. The same procedure as that described above for **1c** was followed, except **4a** (5.99 g, 0.03 mol) was used instead of **1a**. The product was obtained as brown liquid at room temperature. Yield: 6.4 g, 85%; mp −71.9 °C. ESI-MS (CH_3OH): positive ion, 164 [C_3CNmim]; negative ion, 87 [BF_4]. ^{1}H NMR (CD_3CN): δ = 8.54 (s, 1H), 7.43 (s, 1H), 7.39 (s, 1H), 4.17 (brs, 2H), 3.83 (s, 3H), 2.44 (brs, 2H), 1.92 (brs, 2H), 1.60 (brs, 2H). ^{13}C NMR (CD_3CN): δ = 139.24, 131.19, 128.02, 126.68, 123.72, 38.69, 31.64, 24.70, 18.64. IR (cm^{-1}): 3161, 3120 (ν_{C-H} aromatic), 2955, 2876 (ν_{C-H} aliphatic), 2247 ($\nu_{C\equiv N}$), 1575 ($\nu_{C=N}$). Anal. Calcd for $C_9H_{14}N_3BF_4$ (%): C 43.06, H 5.62, N 16.74. Found: C 43.12, H 5.53, N 16.70.

Synthesis of [C_3CNdimim]Cl 5a. A mixture of 1,2-dimethylimidazole (9.61 g, 0.10 mol) and $Cl(CH_2)_3CN$ (12.43 g, 0.12 mol) was stirred at 100 °C for 24 h. Two phases were formed at the end of the reaction. The upper phase was decanted, and the lower phase was washed with diethyl ether (3 × 30 mL). A pale yellow solid was formed during the washing, and the product was dried in a vacuum for 24 h at RT. Yield: 18.6 g, 93%; mp 105 °C. ESI-MS (CH_3OH): positive ion, 164 [C_3CNdimim]; negative ion, 35 [Cl]. ^{1}H NMR (CD_3CN): δ = 7.50 (s, 1H), 7.31 (s, 1H), 4.14 (t, J(H,H) = 7.17 Hz, 2H), 3.71 (s, 3H), 2.53 (s, 3H), 2.46 (t, J(H,H) = 7.17 Hz, 2H), 2.11 (m, J(H,H) = 7.17 Hz, 2H). ^{13}C NMR (CD_3CN): δ = 125.52, 123.70, 122.32, 120.73, 49.47, 37.66, 28.12, 16.50, 11.92. IR (cm^{-1}): 3182, 3098, 3046 (ν_{C-H} aromatic), 2989, 2898, 2834 (ν_{C-H} aliphatic), 2240 ($\nu_{C\equiv N}$), 1631 ($\nu_{C=N}$). Anal. Calcd for $C_9H_{14}ClN_3$ (%): C 54.13, H 7.07, N 21.04. Found: C 54.18, H 7.17, N 20.92.

Synthesis of [C_3CNdimim]PF_6 5b. The same procedure as that described above for **1b** was followed, except **5a** (5.99 g, 0.03 mol) was used instead of **1a**. The product was obtained as white solid at room temperature. Yield: 7.33 g, 79%; mp 85 °C. ESI-MS (CH_3OH): positive ion, 164 [C_3CNdimim]; negative ion, 145 [PF_6]. ^{1}H NMR (CD_3CN): δ = 7.34 (s, 1H), 7.32 (s, 1H), 4.18 (t, J(H,H) = 7.17 Hz, 2H), 3.75 (s, 3H), 2.55 (s, 3H), 2.51 (t, J(H,H) = 7.17 Hz, 2H), 2.14 (m, J(H,H) = 7.17, 2H). ^{13}C NMR (CD_3CN): δ = 144.91, 122.87, 120.99, 120.59, 46.85, 35.08, 25.02, 14.09, 9.37. ^{31}P NMR (CD_3CN): −140.80 (hept). IR (cm^{-1}): 3150 (ν_{C-H} aromatic), 2966 (ν_{C-H} aliphatic), 2249 ($\nu_{C\equiv N}$), 1628 ($\nu_{C=N}$). Anal. Calcd for $C_9F_6H_{14}N_3P$ (%): C 34.96, H 4.56, N 13.59. Found: C 35.02, H 4.52, N 13.61.

Synthesis of [C_3CNdimim]BF_4 5c. The same procedure as that described above for **1c** was followed, except **5a** (5.99 g, 0.03 mol) was used instead of **1a**. The product was obtained as white waxy solid at room temperature. Yield: 6.77 g, 90%; mp 40 °C. ESI-MS (CH_3OH): positive ion, 164 [C_3CNdimim]; negative ion, 87 [BF_4]. ^{1}H NMR (CD_3CN): δ = 7.31 (s, 1H), 7.30 (s, 1H), 4.15 (t, J(H,H) = 6.84 Hz, 2H), 3.72 (s, 3H), 2.59 (s, 3H), 2.47 (t, J(H,H) = 6.84, 2H), 2.13 (m, J(H,H) = 6.84, 2H). ^{13}C NMR (CD_3CN): δ = 125.54, 123.70, 122.08, 120.52, 49.51, 37.71, 28.04, 16.59, 11.98. IR (cm^{-1}): 3185, 3145 (ν_{C-H} aromatic), 2966 (ν_{C-H} aliphatic), 2244 ($\nu_{C\equiv N}$), 1701 (($\nu_{C=N}$). Anal. Calcd for $C_9H_{14}BF_4N_3$ (%): C 43.06, H 5.62, N 16.74. Found: C 42.85, H 5.75, N 16.68.

Synthesis of [Pd(N$\equiv$CC_3dimim)$_2$$Cl_2$][$BF_4$]$_2$. A mixture of **5c** (153 mg, 0.61 mmol) and palladium chloride (54 mg, 0.305 mmol) in 5.0 mL of dichloromethane was stirred at RT for 3 days. The resulting yellow solid was extracted by filtration, washed with diethyl ether (2 × 5.0 mL), and dried in a vacuum. Yield: 195 mg, 94%; mp 130 °C. ^{1}H NMR (DMSO): δ = 7.62 (s, 1H), 7.61 (s, 1H), 4.16 (t, J(H,H) = 7.17 Hz, 2H), 3.72 (s, 3H), 2.57 (s, 3H), 2.56 (brs, 2H), 2.06 (m, J(H,H) = 7.17 Hz, 2H). ^{13}C NMR (DMSO): δ = 148.10, 125.91, 124.20, 123.16, 49.61, 38.09, 28.39, 16.81 and 12.60. IR (cm^{-1}): 3152 and 3120 (ν_{C-H} aromatic), 2988, 2973 and 2901 (ν_{C-H} aliphatic), 2325 ($\nu_{C\equiv N}$), 1692 ($\nu_{C=N}$). Anal. Calcd for $C_{18}H_{28}B_2Cl_2F_8N_6Pd$ (%): C 31.82, H 4.15, N 12.37. Found: C 31.75, H 4.10, N 12.34.

Hydrogenation Reactions. Hydrogenations were carried out in the same way as described previously.[44] $PdCl_2$ (5.0 mg) was dissolved in ionic liquid (1.0 mL) to afford [Pd(N$\equiv$CC_3dimim)$_2$$Cl_2$]-[$BF_4$]$_2$ (see above), and 1,3-cyclohexadiene (1.0 mL) was added. The multicell autoclave was pressurized with H_2 to 45 atm, sealed, and heated to 100 °C for 4 h. The products were identified using a combination of GC versus known standards and ^{13}C NMR spectroscopy. Turnover frequencies are quoted in number of moles of substrate converted per mole of catalyst per hour.

X-ray Structure Determination. Data collections were performed at 140 K on a four-circle kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD for compounds **1a** and **5b**. Diffraction data for **3a** and **3b** were measured at 140 K on a marresearch mar345 IPDS. Data reduction was carried out with CrysAlis RED, release 1.6.9.[45] Absorption correction[46] has been applied to data sets belonging to **3b**. Structure solution and refinement as well as molecular graphics and geometric calculations were performed for all structures with the SHELXTL software package, release 5.1.[47] The structures were refined using the full-matrix least squares on F^2 with all non-H atoms anisotropically

(44) Daguenet, C.; Dyson, P. J. *Catal. Commun*. **2003**, *4*, 153.
(45) Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, 2002.
(46) Walker, N.; Stuart, D. DELABS. *Acta Crystallogr., Sect. A* **1983**, *39*, 158−166.
(47) Sheldrick, G. M. University of Göttingen, Germany, 1997; Bruker AXS, Inc., Madison, WI, 1997.

defined. H atoms were placed in calculated positions using the "riding model".

Acknowledgment. We thank the EPFL and Swiss National Science Foundation for financial support.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034801P